

ARMY RESEARCH LABORATORY



Hydrogen Plasma Removal of Military Paints: Chemical Characterization of Samples

by P. J. Kaste, R. G. Daniel, R. A. Pesce-Rodriguez,
M. A. Schroeder, and J. A. Escarsega

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Abstract

A moderate temperature hydrogen plasma has been developed for removal of chemical-agent-resistant (CARC) propellant coatings, and the chemistry and morphology of the CARC removal process has been investigated. A microwave-based plasma generator, producing a low-temperature atomic beam was used to treat the samples. The plasma heats the sample only 10–20° C. Additional heat was supplied to maintain temperatures of 200–300° C. Helium and hydrogen plasmas were studied in this effort. However, helium was not at all effective, showing that atomic bombardment alone is not sufficient to remove the paint, and that chemical reactivity is needed. One of the CARC paints studied, a conventional formulation, is on the qualified products list, while the other two formulations are experimental. Paint variables that were studied include: one- and two-pack formulations; moisture-cured and water-reducible chemistries; aluminum with chromate, and steel with zinc phosphate conversion coatings; and presence or absence of an adhesive epoxy sublayer. The samples were characterized by microreflectance and photoacoustic Fourier-transform infrared spectroscopies. Heat treatment to 300° C resulted in some degradation of the conventional CARC, but the experimental CARC was mostly unaffected. The hydrogen plasma removed up to 50 weight-percent of the CARC layers, but was much more effective in degrading the conventional formulation. Virtually all of the urea, amine, and polyurethane (present in the resin as a prepolymer) functional groups were removed by the H-plasma in the case of the conventional propellant, whereas in the experimental paints, these groups were only slightly reduced.

Acknowledgments

Shirley Liebman is thanked for providing helpful discussions and reference material on polyurethane infrared spectral band assignments. The Environmental Quality Basic Research Program provided financial support for this work.

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1. Background

Reducing the hazardous wastes generated in paint maintenance procedures for military vehicles is imperative for compliance with Occupational Safety and Health Agency (OSHA) regulations. A particularly effective means of paint removal (commonly referred to as depainting) is immersion in methylene chloride, and for many years, this has been a standard method. However, methylene chloride is unacceptable by current OSHA guidelines. The goal now is to rapidly develop new technologies that will minimize volatile organic compounds (VOCs) and hazardous pollutants, with a concomitant reduction in disposal cost. Across the Department of Defense (DOD), the problem is huge. Within the Army alone, 2,000 tons of depainting wastes have been reported at 16 locations for the Industrial Operations Command, the Army's major producer of hazardous waste (Holst 1997).

The purpose of this effort is to determine the effectiveness of a mild-temperature hydrogen plasma (less than 300° C) for removal of paints currently used on military vehicles, as well as for paints being formulated for future use. To this end, paint samples are being characterized prior to, and after, plasma treatment. Knowledge of the residue composition after treatment will assist in understanding the plasma-paint interaction mechanisms and will provide a basis for altering the plasma properties and improving paint removal. Both conventional and advanced formulations were studied in this effort. Improved paint formulations may offer advantages of improved adhesion and are thus attractive for vehicles and aircraft. However, improved adhesion can also render them difficult to remove for periodic maintenance; thus, an understanding of the plasma interaction mechanisms involved with fielded and candidate paint formulations is essential.

In hydrogen atom plasmas, catalytic depolymerization can occur by H-atom attack on carbon in the polymer to produce a carbon-centered radical. Beta-scission of the radical results in formation of a fragment and a new radical, allowing "unzipping" of a hydrocarbon backbone. If the fragment generated is sufficiently large, recovery of products that can be readily recycled into monomers might be possible, thereby reducing life-cycle costs. However, hydrocarbon chains are only one facet of paint chemistry. Other bonds are a complex mixture of organic and inorganic chemistries that

influence the overall structure-property relationships. In this work, the effectiveness of mild-temperature atomic hydrogen plasmas in breaking down the highly cross-linkable paint structures will be examined. High-temperature paint removal procedures have the disadvantage that they can result in hydrogen embrittlement of the metal surface and therefore degrade mechanical properties. The mild temperatures used in this study will help circumvent the hydrogen embrittlement problem.

2. Paint Formulations

The paints studied are polyisocyanate-based formulations typical of commercial and military vehicles. There are two basic types: (1) one-pack moisture-cured formulations, and (2) two-pack water-reducible formulations (Turner 1988). In both types, 1,6-hexamethylene diisocyanate (HDI) is the major ingredient and is present in the cyanurate form, a cyclic trimer with substituted 1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, shown in Figure 1. This is a nonvolatile, stable form of the isocyanate, which minimizes the hazardous properties associated with volatile isocyanate monomers. A description of the compositions of the paints follow.

Ref: HU4293 1,3,5-TRIS-ISOCYANATOHEXAMETHYLENE ISOCYANURATE

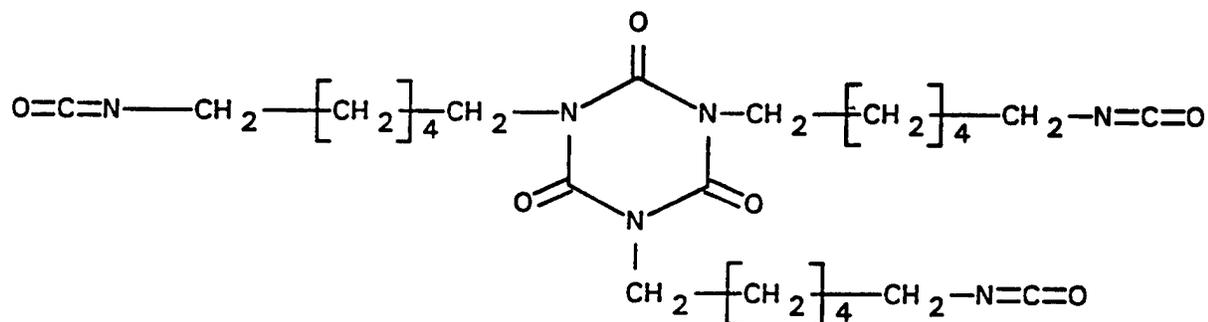


Figure 1. Structure of HDI Isocyanurate.

2.1 Standard One-Pack Moisture-Cured Paints. The one-pack formulation relies on moisture from the environment to react with isocyanate groups to first form carbamic acid, which is unstable and converts rapidly to an amine with release of CO₂ (Figure 2a); this reaction does not result in chain cross-linking and polymerization. The CO₂ released in the paint polymerization process occurs at a sufficiently slow rate so that bubble formation and popping do not occur. Drying is faster if the molecular size of the initial isocyanate compounds is large. Further reaction of the amine with another polyisocyanate group results in polymerization with the formation of a monosubstituted urea (Figure 2b). The latter may react with atmospheric water, and polymerization is extended. The rate of polymerization is very dependent on temperature (controlling the rate of amine to urea formation) and, to a lesser extent, the humidity. Moisture in the sample must be excluded so that the paint does not harden in the container, and the cans must be kept well sealed. Pigments, which characteristically hold water strongly, are prereacted with monomers of isophorone diisocyanate to scavenge water. Residual diisocyanate monomer is eliminated by reaction with a polyester resin prior to paint manufacture. Typical characteristics of one-pack polyurethane paints are: (1) the reactive components exist as low-molecular-weight polymers in the can, (2) they usually contain a medium to high solids loading (35 weight-percent or greater), and (3) cross-linking proceeds slowly when exposed to air (particularly in cold weather) unless conditions are controlled.

One-pack paints do not form polyurethane cross-links, since no components containing free hydroxyl groups are present. However, a polyurethane prepolymer may be present in the packaged, uncured material. In this effort, two different one-pack formulations were studied. The first was a qualified products list (QPL) item, meaning that it yielded acceptable results in a series of standard tests. This formulation has also been used on fielded vehicles. The material available was tan in color, although in general any military camouflage can be made by changing the pigments. This paint contained silica-based solids as fill material; it also contained a substantial (proprietary) level of polyurethane in the prepolymer resin (Urs 1998). Throughout this report, this formulation will be referred to as the standard one-pack paint.

The second one-pack formulation was an experimental paint that contained glass beads as the solids fill material. It has quite different physical and chemical characteristics than the standard one-

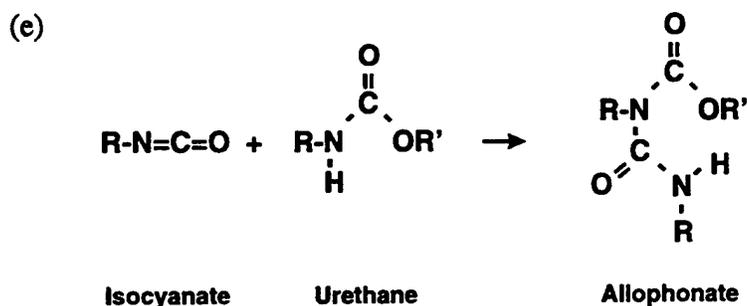
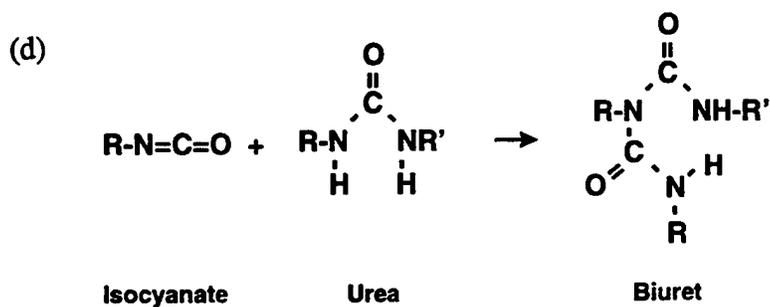
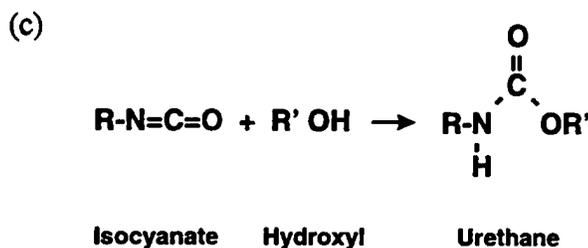
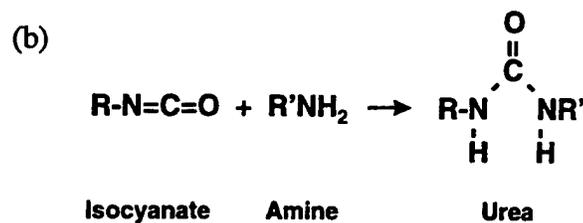
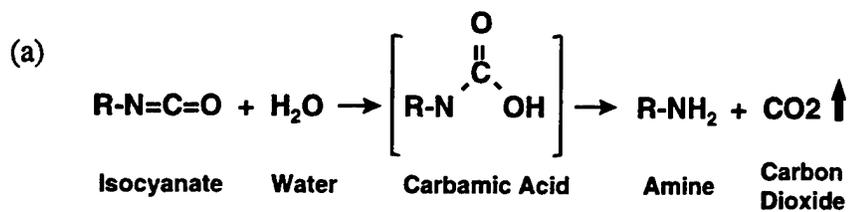


Figure 2. Isocyanate Reactions in Paint Curing: (a) With Water to Form the Amine, (b) With the Amine to Form the Urea, (c) With a Polyol to Form the Polyurethane, (d) With Urea to Form the Biuret, and (e) With Polyurethane to Form the Allophanate, Respectively.

pack paint. The reasons for the differences are not yet totally understood. In addition to containing different solids fill material, the manufacturing sources of the resin prepolymer for the two formulations are different. The prepolymer compositions have a strong affect on paint properties and are therefore usually proprietary. Thus, different resin compositions could play an important role in the different properties observed in the two formulations. This formulation will be referred to as the experimental one-pack formulation throughout this report.

2.2 Experimental Water-Reducible Two-Pack Paints. In the two-pack formulation, the polyisocyanate is contained in one pack, while a second pack contains the polyol resin, which reacts with the polyisocyanate to form polyurethane (Figure 2c). One- and two-pack paints based on an isocyanate could be expected to be quite different, since the one-pack paint can only form urea bonds and the two-pack can form polyurethane bonds. However, the two-pack paints used in this study are compositionally very similar to the one-pack paints. In the two-pack paints, excess isocyanate groups are present relative to the number of polyol hydroxyl groups (i.e., the paint is said to be "highly indexed"). Thus, in addition to containing polyurethane, there is a substantial amount of urea present in the paint from reaction with atmospheric moisture. Since the one-pack paints with urea bonds actually contain a substantial (proprietary) amount of a polyurethane prepolymer, the difference in the one- and two-pack water-reducible paints is subtle.

The two-pack paints are formed by mixing two fractions just prior to application. The first fraction is pigmented and contains over 50% by weight proprietary components, including the polyol, which reacts with the isocyanate to form the polyurethane. Polyols used in manufacturing polyurethanes and some polyisocyanurates are generally either polyesters or polyethers, terminated by hydroxyl groups with which the isocyanate group reacts during polymerization. Polyols tend to be viscous liquids at room temperature and have low volatility. The polyol fraction also contains the solids fill: 10–15 weight-percent each of silica (silicon dioxide, SiO_2) and talc (magnesium silicate, $\text{Mg}_3\text{SiO}_4\text{O}_{10}(\text{H}_2\text{O})$). The second fraction contains 50–75 weight-percent of the isocyanate, as well as 20–30 weight-percent of an ester of oxo-alcohol. Both fractions can be dispersed in aqueous environments for admixing and viscosity adjustments. The two-pack paints have a relatively short pot life and need to be applied shortly after mixing. There is much interest in the two-pack paints

because their volatile organic content is less than half that of the conventional one-pack paints. The urethane-containing paints (one- and two-pack) are inherently very tough and resistant to abrasion and chemical exposure. Both the urea and polyurethane functional groups have an active hydrogen, which can further react with isocyanate to form the biuret and allophanate, respectively (Figures 2d and e). Thus, the polymerized paint structure may be quite complex.

2.3 Paint Substrates. The standard one-pack paint was applied to aluminum coupons that had been treated with a copper chromate conversion coating to facilitate paint adhesion and resist corrosion. The experimental one- and two-pack paints were applied to steel coupons that had been treated with a zinc phosphate conversion coating. In the case of the experimental one-pack paint, an epoxy primer was applied between it and the conversion coating. The epoxy acts as a bonding agent, forming a tight adhesion to the paint and the conversion coating. On fielded vehicles, the epoxy is applied after the conversion coating. When the epoxy has dried for a minimum of 2 hr, the top coat is sprayed on. The epoxy primer was used only with the experimental one-pack paint. All paint samples contain inorganic pigments and a high (nominally, 20–40% by weight) solids fill of silica and/or talc. The three paints studied in this effort are listed in Table 1.

Table 1. Description of the Three Paints Used in This Study

Paint Type	Experimental	Substrate/Conversion Coating	Epoxy Primer
One-Pack, Moisture-Cured	No, standard	Al/Cu ₄ (CrO ₄) ₂	No
One-Pack, Moisture-Cured	Yes	Steel/Zn ₃ (PO ₄) ₂	Yes
Two-Pack, Water-Reducible	Yes	Steel/Zn ₃ (PO ₄) ₂	No

3. Experimental

3.1 Plasma Treatment. Samples were prepared by spray methods according to military specifications onto metal plates about 20 cm long and 13 cm wide. From this stock material, coupons were cut that were about 2 cm by 1.5 cm; care was taken to obtain representative samples and avoid edge effects. The paint coupons were treated in a chamber operated at reduced pressure, which ensured a reproducible atomic beam. The atomic beam is generated by passing the feed gas, either inert argon or reactive hydrogen or oxygen, through a microwave discharge. The concentration of the feed gas determines the properties of the plasma and thus the atomic beam. The paint sample is placed on a mount capable of being heated. This allows the dependence of temperature to be studied, as the plasma treatment alone heats the sample by only 10 or 20° C. Samples studied in this effort were either treated with heat alone or treated with heat and plasma. For brevity, throughout the report, the combined heat and plasma treatment will be referred to as "plasma" treated, although heating up to 300° C is implied.

Argon was not effective in eliminating the paint. This shows that atomic bombardment with this inert chemical material, under these conditions, is not sufficient and that chemical reaction with the paint is needed. Because different analytical and spectroscopic sampling methods and paint chemistries were used in the hydrogen and oxygen plasma efforts, for clarity, this report will focus on the hydrogen plasma results only; the oxygen plasma results will be presented in a separate report.

3.2 Sample Characterization. Samples were characterized before and after treatment by infrared (IR) spectroscopy and microscopy.

3.2.1 Fourier-Transform Infrared (FTIR) Spectroscopy. From vibrational spectra, it is possible to identify functional groups present in the material. Microreflectance FTIR was used to obtain spectra of the surface (i.e., about 10 μ) of materials, and photoacoustic spectroscopy (PAS) was used to sample below the surface. These sampling methods offer the advantage of being nondestructive. The reflectance spectra were obtained using a Spectra-Tech microreflectance attachment and were

run at 4 cm^{-1} resolution, 200 scans signal averaged. The spectrometer used for all the IR measurements was a Mattson Polaris. The photoacoustic spectra were obtained with an MTEC Photoacoustics, Inc. (Ames, IO), Model 100 detector run at 8 cm^{-1} resolution, 100 scans signal averaged.

In PAS, a mirror directs the IR beam onto the sample and heats it. The IR beam is modulated, and the heating of the gas layer above the sample contracts and expands at the same frequency as the modulated IR beam. This generates a sound wave that is detected with a microphone, and the signal is processed by the FTIR detector electronics. The sample chamber and microphone are sealed and purged during operation with a high thermal conductivity gas, typically He, to maximize sensitivity (Figure 3) (McClelland 1993). Sample spectra are usually ratioed against a spectrum from a totally absorbing material, such as carbon black.

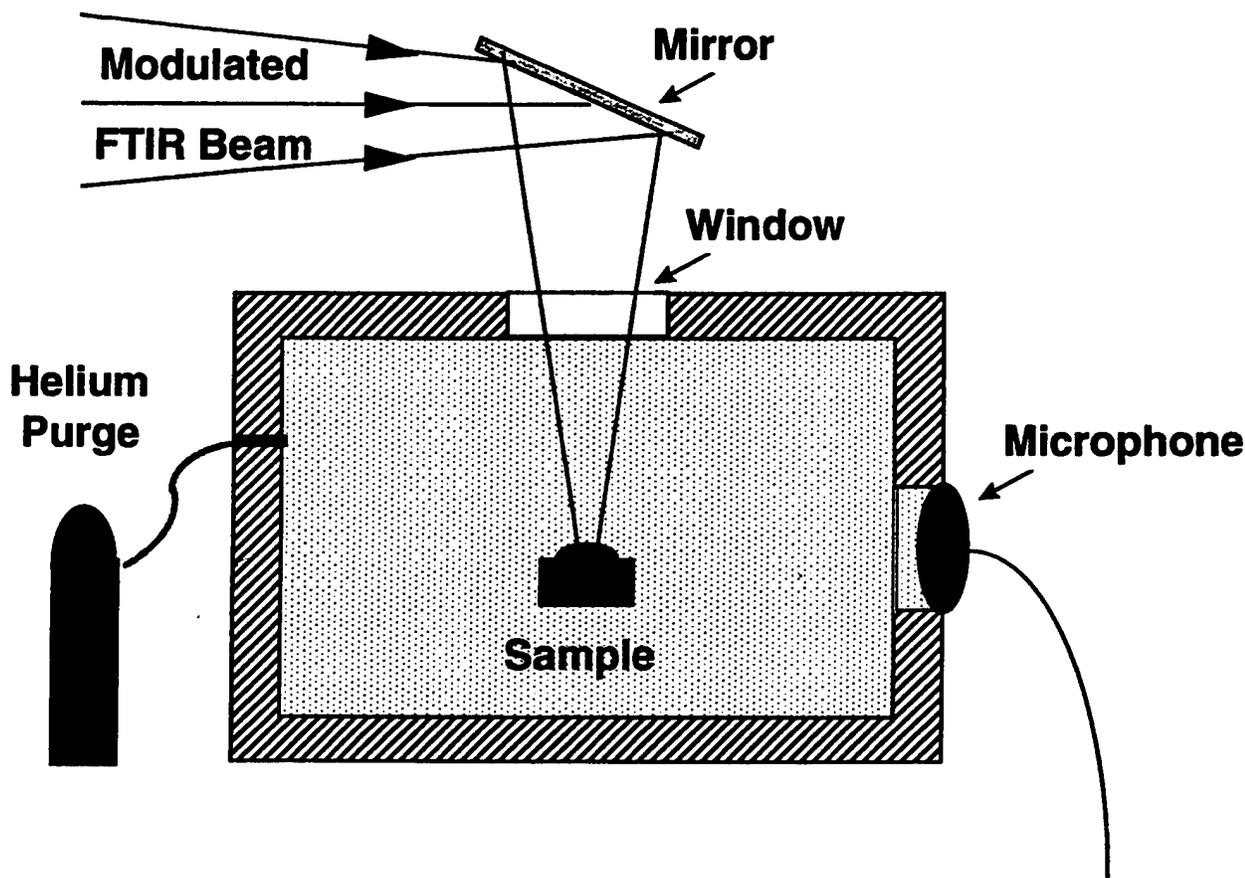
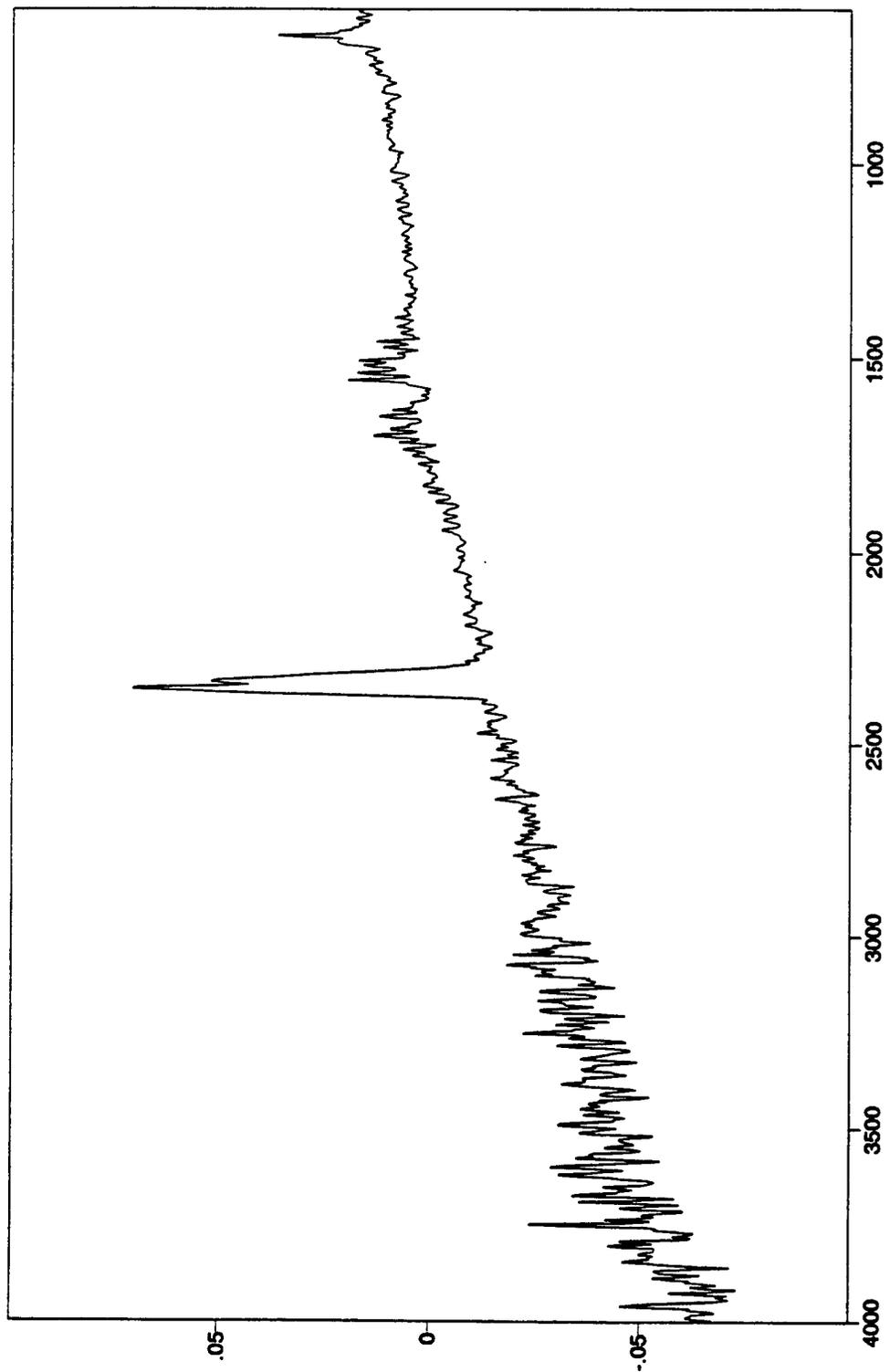


Figure 3. Schematic of PAS Detector.

Penetration depth is a function of the thermal conductivity and heat capacity of the sample, and modulation frequency of the spectrometer; multiple modulation frequencies are typically available. The modulation frequency, in turn, varies with wavenumber and is 10 times greater at 400 cm^{-1} than at 4000 cm^{-1} , a normal mid-IR operating range. Thus, by varying the mirror velocity, depth profiling can be achieved: the slower the mirror velocity, the greater the penetration depth. Because the penetration depth varies with wavenumber, differences in relative intensities between PAS and transmission spectra are observed. Band frequencies are the same, however, so that standard IR correlation tables are valid.

The available PAS accessory was in need of refurbishment, and spectra obtained were not optimal. For example, it was not possible to obtain a stable signal at various mirror velocities with the paint samples, and thus, profiling the sample as a function of depth of radiation penetration was not possible. The only mirror speed successfully used was 0.115 cm/s . It was possible to obtain background measurements of carbon black and some low IR-absorbing samples at other mirror speeds, but not of the paint samples. Note that although depth profiling was not achieved, the PAS technique probes at and below the surface (i.e., greater than $10\text{ }\mu\text{m}$, as opposed to the reflectance method, which nominally samples only the top few microns). The noise level varied significantly across the spectral region obtained ($4000\text{--}600\text{ cm}^{-1}$), as indicated from the hundred-percent line (HPL) taken of background samples of carbon black (Figure 4). Above 3000 cm^{-1} , the peak-to-peak noise level (PPNL) was ± 2.5 units, improving significantly at about 3000 cm^{-1} to ± 1.5 ; below 2300 cm^{-1} , the PPNL was as low as ± 0.4 .

3.2.2 Optical and Scanning Electron Microscopy (SEM). SEM enables profiling of the morphology of the sample, including nature and distribution of the solids fill within the matrix, adhesion of the paint polymer to the inorganic particles and presence of porosity of the polymer. Micrographs were obtained using a JEOL 820 scanning electron microscope. The thickness, uniformity, and porosity of the paint and primer layers were assessed with an optical microscope.



Absorbance / Wavenumber (cm-1)

File # 1 = HPLHE2

E:\PAMIPAS\WRPAIN\TJAN9\cb1he

Res= 8cm-1

Figure 4. PAS-IR Hundred-Percent Line.

4. Results

4.1 Photoacoustic IR Spectroscopy

4.1.1 Standard One-Pack Moisture-Cured Paint Samples. Virgin samples of the standard one-pack paints were tan in color but, upon relatively mild treatment (heating in vacuum to 200° C), turned brick red. With hydrogen plasma treatment and simultaneously heating to 200° C, the samples turned a gray-black or charcoal color. Weight loss after plasma treatment was nominally 50%. The PAS spectra of the virgin and treated one-pack paint samples are shown in Figures 5–7: (a) Figure 5 is the untreated tan sample; (b) Figure 6 is the sample after heat treatment under vacuum; and (c) Figure 7 is the plasma and heat-treated sample. Some peak assignments of importance in filled isocyanate paints are provided in Table 2 as an aid to interpreting the spectra. Further details of these assignments as pertinent to paint spectral features are provided as follows.

- $3650\text{--}3450\text{ cm}^{-1}$: Broad hydrogen bonds of OH can arise from the polyol. This band diminishes as the polyol reacts with the isocyanate to form the urethane cross-link. Proprietary ingredients, such as carboxylic acids, absorb here as well.
- $3440\text{--}3200\text{ cm}^{-1}$: In paint spectra, the NH and/or NH₂ stretch can arise from urea, polyurethane, or amines. In the PAS spectra, these bands are superimposed on sloping baselines in an area of low signal to noise (S/N); thus, this spectral region is better probed using reflectance spectroscopy (discussed below).
- $2930\text{--}2860\text{ cm}^{-1}$: C-H asymmetric stretch (2930 cm^{-1}) and symmetric stretch (2860 cm^{-1}). This band is relatively strong in the spectra of all the intact paints, due to the contribution of six methylene groups per diisocyanate molecule.
- $1765\text{--}1775\text{ cm}^{-1}$: Esters with an aromatic ring on the carbonyl absorb here. Polyols with aromatic esters are not uncommon in isocyanate-based paint formulations.

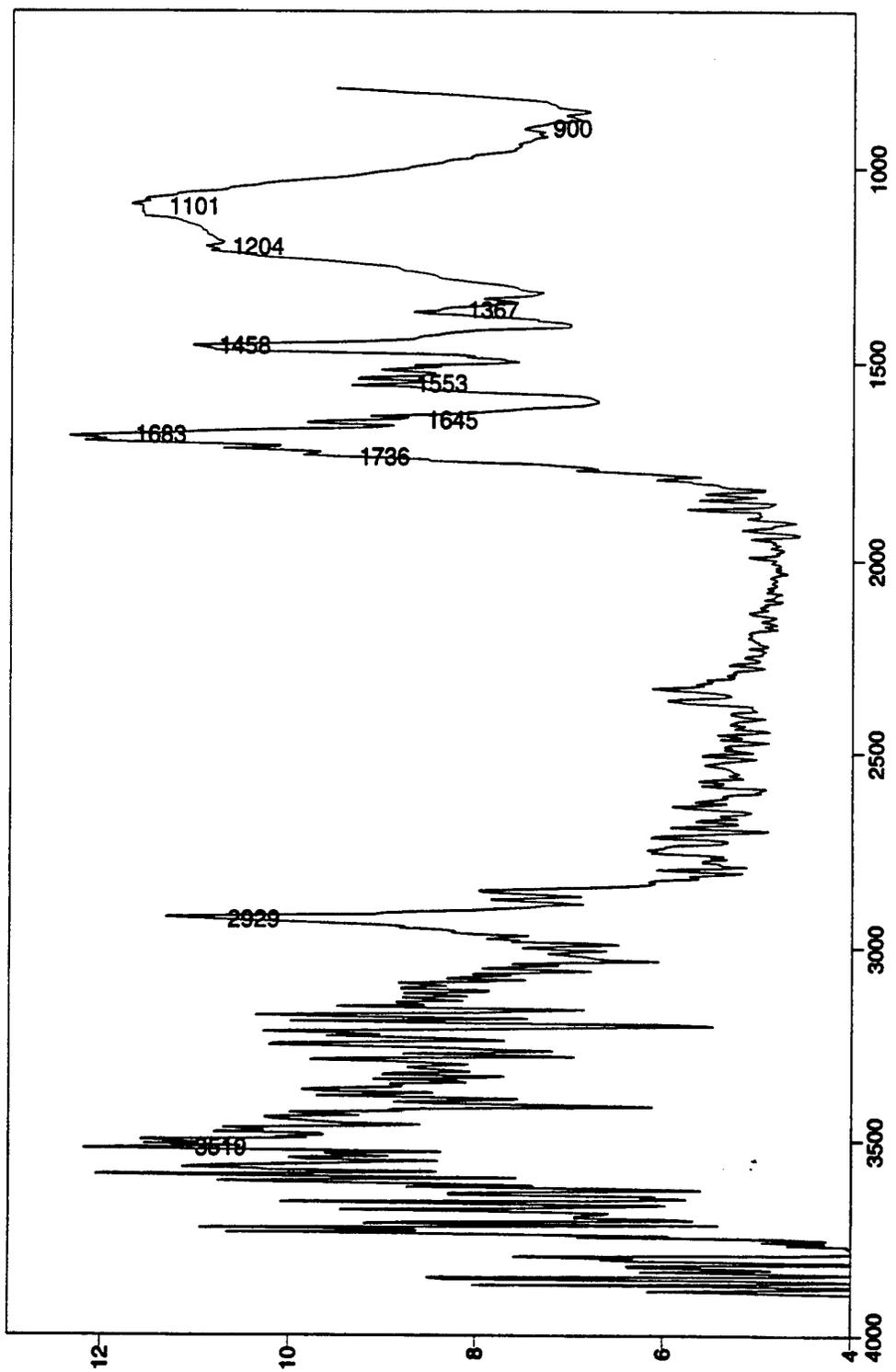
- *1760–1720 cm⁻¹*: These carbonyl bands appear as shoulders on the high-frequency side of the more-dominant 1700 cm⁻¹. These could be due to the urethane carbonyl, either as a paint-curing product or from urethanes present in the prepolymer or from several proprietary components containing other carbonyl functional groups. For example, in the standard tan one-pack paint, carbonyls, such as polycarboxylic acids, fatty acids, and saturated polyester-polyols, could comprise up to 10 weight-percent of the cured sample. Pigments and their associated dispersants could also absorb in this region.
- *1685 cm⁻¹*: The isocyanurate carbonyl absorbs very strongly at 1685 cm⁻¹, due to the three carbonyls in the six-membered ring. Refer to Figure 8, a Sadtler (Sadtler Research Laboratories, Inc, Philadelphia, PA) reference spectrum of HDI, also referred to as 1,3,5-tris-isocyanatohexamethylene isocyanurate.
- *1635–1655 cm⁻¹*: Bands in this region are most likely due to the C = O stretch from a urea. If amines are present, an NH₂ deformation band could also contribute.
- *1560–1510 cm⁻¹*: Amide II band, which is due to the coupling of the NH deformation and the C-N stretching modes (N and H move in opposite direction relative to C). Although common terminology suggests a simple amide, this band is a strong feature in the spectra of ureas or carbamates.
- *1465 cm⁻¹*: Due to the scissoring of methylene groups. Usually this is a moderately weak band. However, due to the presence of three sets of hexamethylene groups in the HDI upon which these paints are based, this is a very prominent spectral feature. Other components containing methylene groups contribute also but are eclipsed by the isocyanurate. The 1465 cm⁻¹ band has a characteristic intensity relative to the 1685 cm⁻¹ ring carbonyl of isocyanurate.
- *1460 cm⁻¹*: When this band is present and there is no 1685 cm⁻¹ band, it is due to an inorganic species containing calcium, such as either calcium hydroxide or calcium carbonate. Figure 9 shows the Sadtler reference spectrum of calcium carbonate.

- $1250\text{--}1000\text{ cm}^{-1}$: Very strong, broad band, due at least, in part, to silica. A representative reference spectrum of silica (Figure 10a) shows a long high-frequency tail that would explain the nonreturn to baseline of peaks up to almost 1800 cm^{-1} . There are various forms of silica with different particle sizes, and band broadness and position vary significantly; however, most are fairly broad and within the $1000\text{--}1250$ region. More than one band may contribute: bands at 1170 , 1220 , and 1280 cm^{-1} , which could arise from ether or aliphatic groups, seem to be superimposed on the silica. Magnesium silicate (talc) absorbs near 1000 cm^{-1} as well, as shown in Figure 10b.

Note that amines are likely to be present if they do not react further with isocyanate to form the urea. However, identification of amines in the presence of other paint components is difficult: (a) the aliphatic NH_2 bands at 3250 and 3450 cm^{-1} are in a region of very low S/N and sloping baseline; (b) the NH_2 deformation at $1600\text{--}1650\text{ cm}^{-1}$ is obscured by the urea carbonyl; and (c) the C-N band absorbs in the $1000\text{--}1200\text{ cm}^{-1}$ region and is obscured by the silica/talc bands.

4.1.1.1 Heat Treatment Under Vacuum. Although the heat/vacuum treatment of the standard one-pack moisture-cured paints causes a strong color change from tan to deep red, the effect on the PAS spectrum is not substantial (Figures 5 and 6). If, during heating, the sample were reacting primarily at the surface exposed to air, the PAS technique, which probes below the surface, would not be sensitive to the change. Band intensities between the untreated and heat-treated samples are basically unchanged, with the exception that the 2860 cm^{-1} band grows relative to the 2930 cm^{-1} band. Both these bands arise from methylene groups, and although changes in their pattern suggest a structural change, or changes in hydrophobic groups in the local environment with which they interact, it is unfortunately of little diagnostic value. It may be possible that the longer hexamethylene groups associate with surface functional groups (e.g., urea) that are changing, creating differences in their band pattern (see section 4.2, Reflectance Spectra).

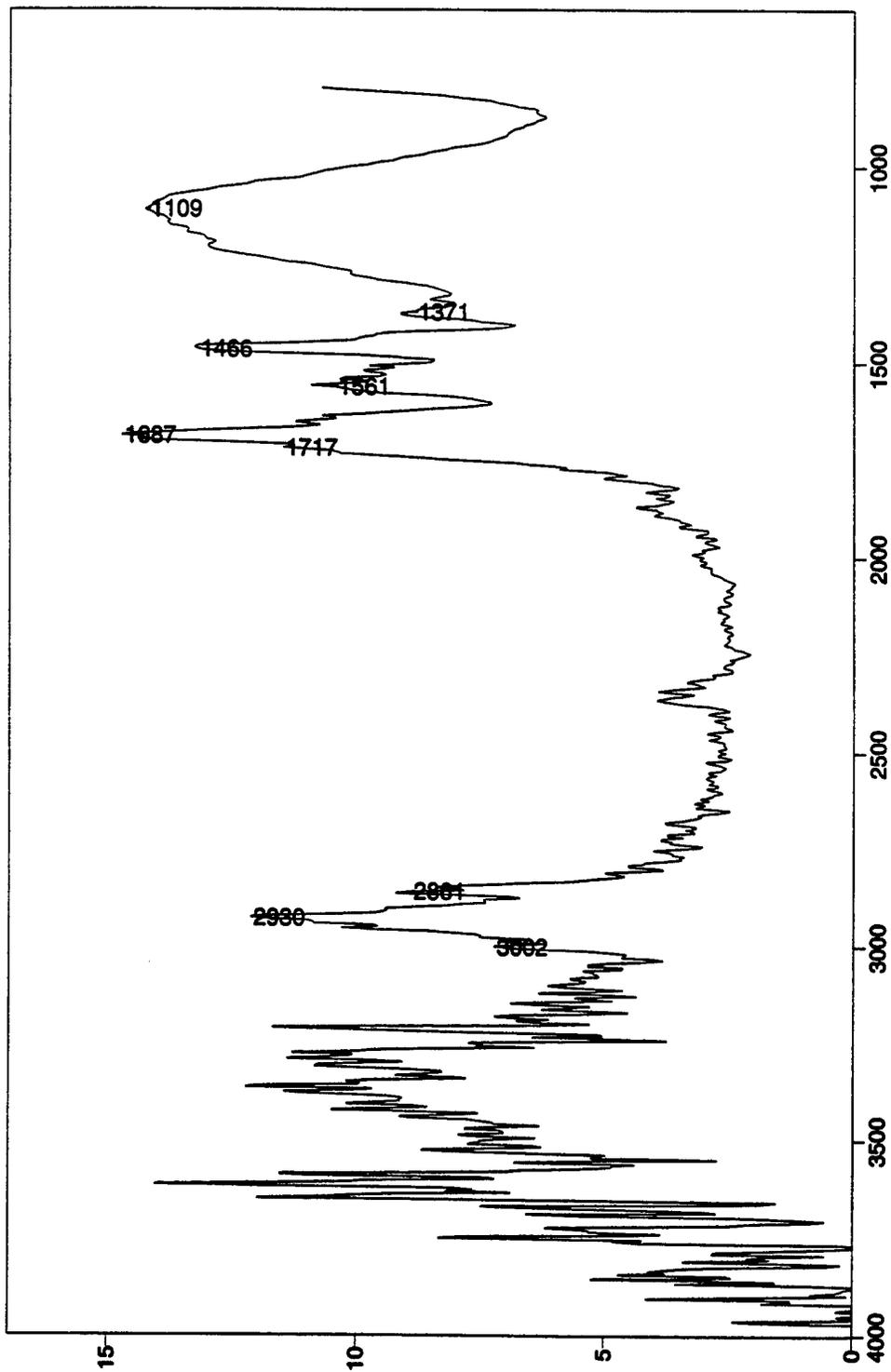
4.1.1.2 Plasma and Heat Treatment. Unlike the heat treatment alone, major spectral changes are observed when the plasma treatment is added (Figure 7). The spectrum is much simplified, indicating loss of functional groups, and consistent with the observation that the sample takes on a



Paged Y-Zoom CURSOR
Res= 8cm-1

Transmittance / Wavenumber (cm-1)
File # 1 = UNP316
E:\PAMPASINOV1896\unp316 max = 0.114288/0.152893

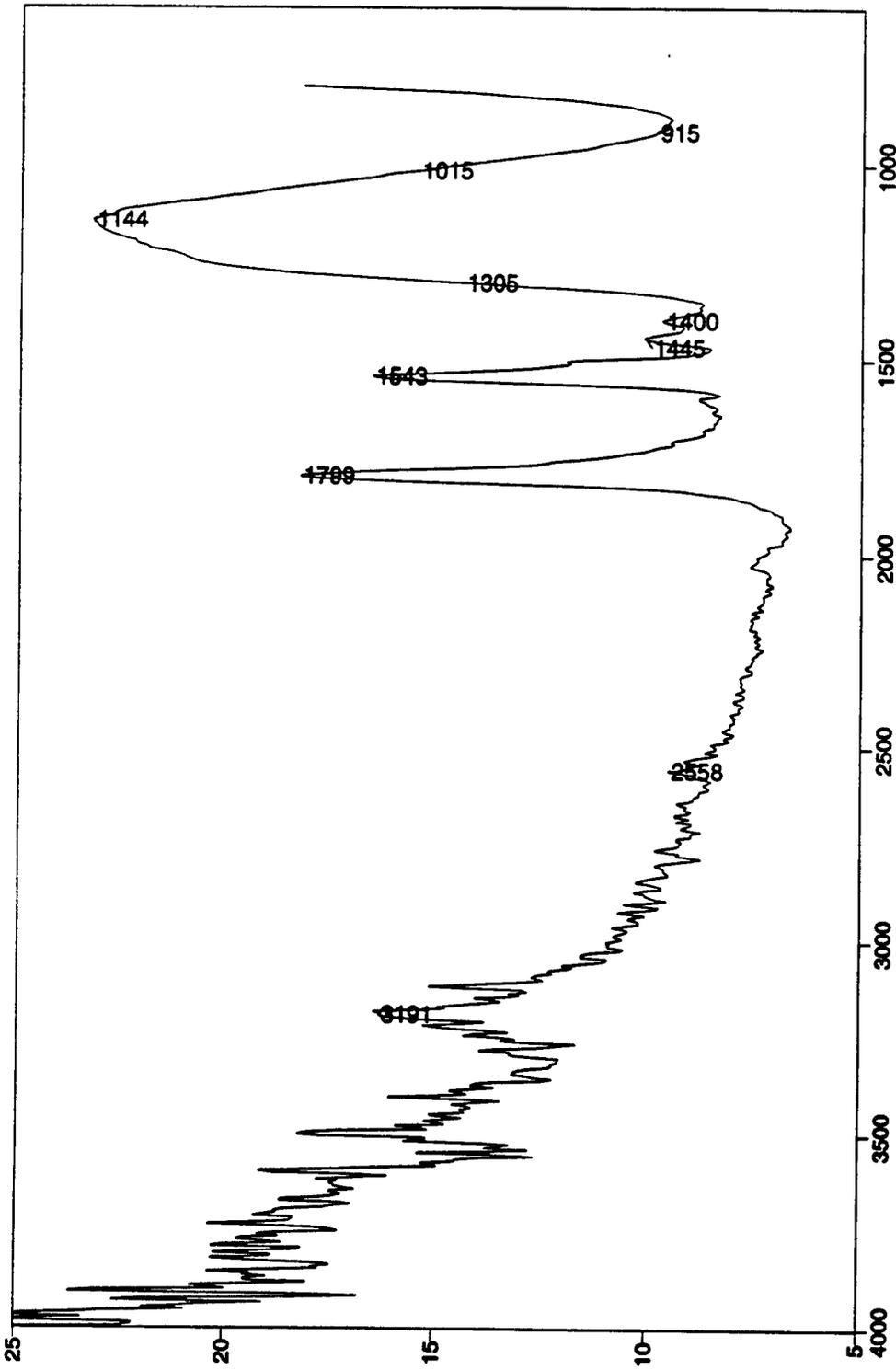
Figure 5. PAS-IR Spectrum of the Untreated One-Pack Tan Paint Sample.



Transmittance / Wavenumber (cm-1) Paged Y-Zoom CURSOR Res= 8cm-1
 File # 1 = RED316

E:\PAMPAS\NOV1896\red316 max = 0.454254/0.525055

Figure 6. PAS-IR Spectrum of the Heat-Treated One-Pack Tan Paint Sample.



Paged Y-Zoom CURSOR
Res= 8cm-1

Transmittance / Wavenumber (cm-1)
File # 1 = PLS316B
E:\PAMPAS\NOV1896\plspnt2 max = 0.804901\0.804901

Figure 7. PAS-IR Spectrum of the Plasma-Treated One-Pack Tan Paint Sample.

Table 2. Spectral Features of Tan Paint Samples

Wavenumber (cm^{-1})	Assignment
3650–3450	OH H-bond
3440–3200	NH and/or NH_2 stretch
2980	CH_3 asymmetric stretch
2930	CH_2 asymmetric stretch
2860	CH_2 symmetric stretch
2280	NCO asymmetric
1765	Polyurethane, aromatic
1720–1740	Polyurethane, aliphatic
1685	Isocyanurate C = O
1650–1690	Urea C = O
1510–1560	Amide II
1465	CH_2 Scissoring
1460	Calcium-oxygen (strong band)
1375	CH_3 -C
1240–1280	Amide III
1250–1000	Silica (strong, very broad)
1220–1000	C-O-C stretch; strong but superimposed over silica band
1000–1250	C-C skeletal vibrations; medium bands superimposed on silica band

charred appearance. The dominant band in the spectrum is broad, peaks at 1110 cm^{-1} , and is due at the low-frequency side (1650 cm^{-1}). Consistent with loss of urea is the loss of the amide II band at 1550 cm^{-1} and the amide III band at $1240\text{--}1280 \text{ cm}^{-1}$. Urea serves to polymerize the tan samples; thus, a loss in urea could result in a charred appearance and loss of integrity of the sample.

The CH_3 absorptions near 3000 and 1375 cm^{-1} are also almost eliminated. These functional groups were not assigned to any compound and could arise from the proprietary material that composes a major portion of the paint, including a polyol. The bands superimposed on that of silica in the virgin and heat-treated samples are also eliminated and include C-C and ether C-O-C bonds.

Thus, except for silica, the spectrum of the residue from plasma/heat treatment is essentially that of the hexamethylene isocyanurate (compare Figures 7 and 8). It is not surprising that inorganic silica

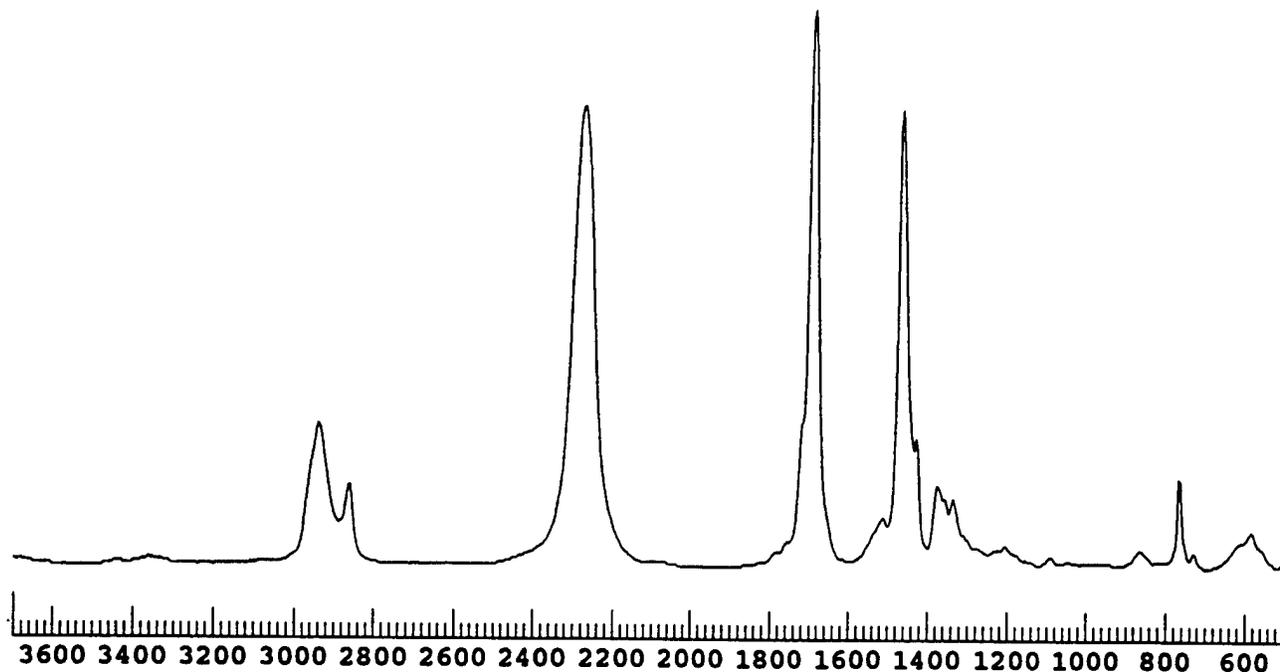


Figure 8. Sadtler Reference Spectrum of HDI.

remains. Although it's well known that the isocyanurate form of HDI is the most nonvolatile and stable, it is interesting that the ring, and even the associated methylene groups, survive the plasma treatment.

In summary, the PAS spectra of the standard one-pack paints showed: (a) heating and vacuum treatment alone causes minimal subsurface reaction although the color change from light tan to brick red is marked, and (b) H-plasma and heat treatment results in elimination of most organic material present (e.g., urea and amines, ethers, some aliphatic groups), with only the silica, and isocyanurate ring with associated hexamethylene groups remaining.

4.1.2 Experimental One- and Two-Pack Water-Reducible Formulations. Virgin samples of two different green paints were provided. Although one paint was a two-component formulation and

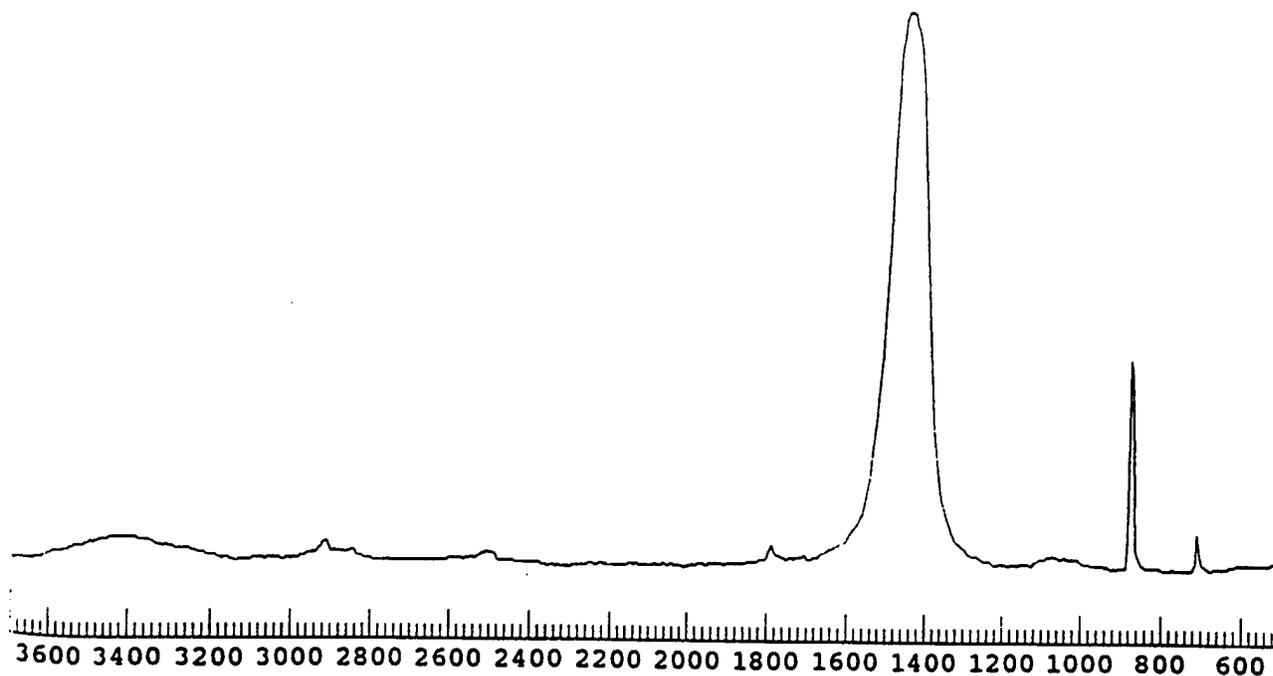
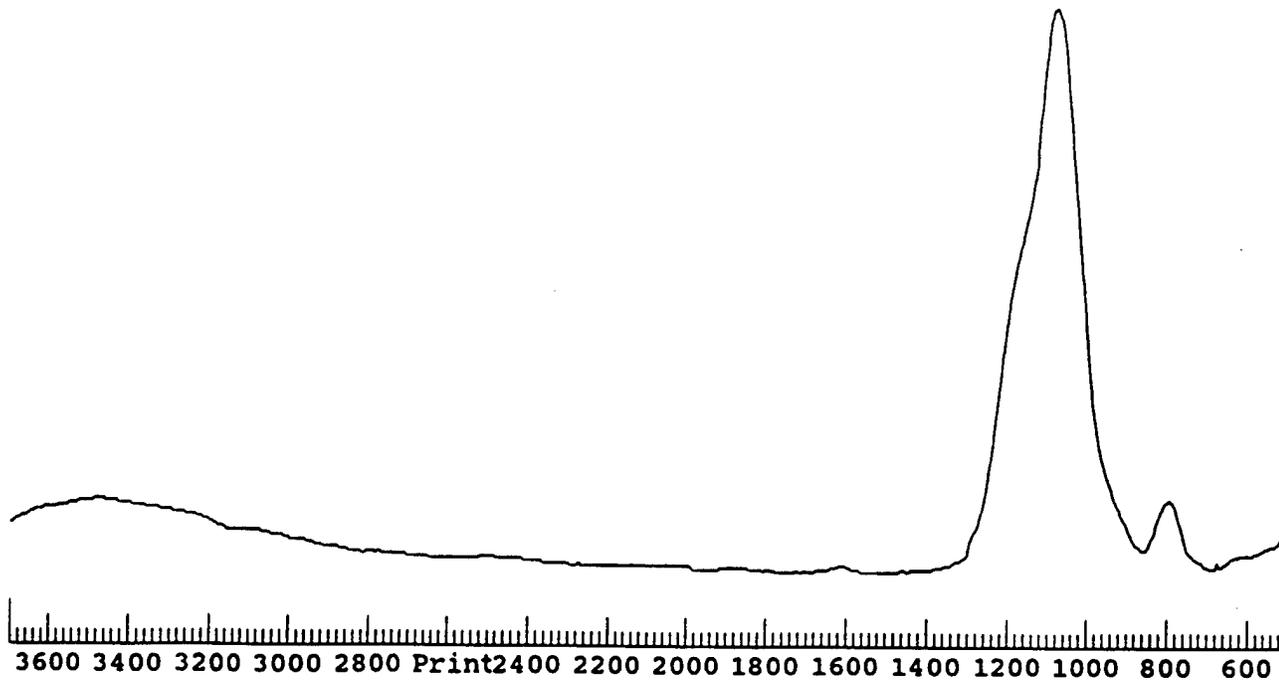


Figure 9. Sadtler Reference Spectrum of Calcium Carbonate.

the other was a one-component formulation, both exhibited similar physical properties and had similar spectral features. Moreover, both were distinctly tougher than the standard tan one-pack paint samples and exhibited different spectral features and response to the plasma. As mentioned previously in Section 2, "Paint Formulations," the one- and two-pack paints are compositionally very similar. Although the one-pack paint forms urea bonds, it contains polyurethane from the polyol prepolymer. And although the two-pack paint forms urethane bonds, since the isocyanate is added in excess, it also forms a significant amount of urea. Thus, both experimental green paints are polyurea/polyurethane formulations and are manufactured by the same company. The morphology of the silica used in the paints differs. The one-pack paint contained glass beads, while the two-pack paint contained amorphous silica and talc. Both green paint samples were exposed to the heat-plasma treatment. The vacuum-heat treatment alone, which was applied to the tan standard samples, was not performed on the green samples. The spectra of the virgin and plasma-treated samples are shown in Figures 11-14.

Ref: PL1168 CAB-O-SIL : 99% SILICON DIOXIDE



Ref: PL1160 EMTAL 41 : MAGNESIUM SILICATE (TALC)

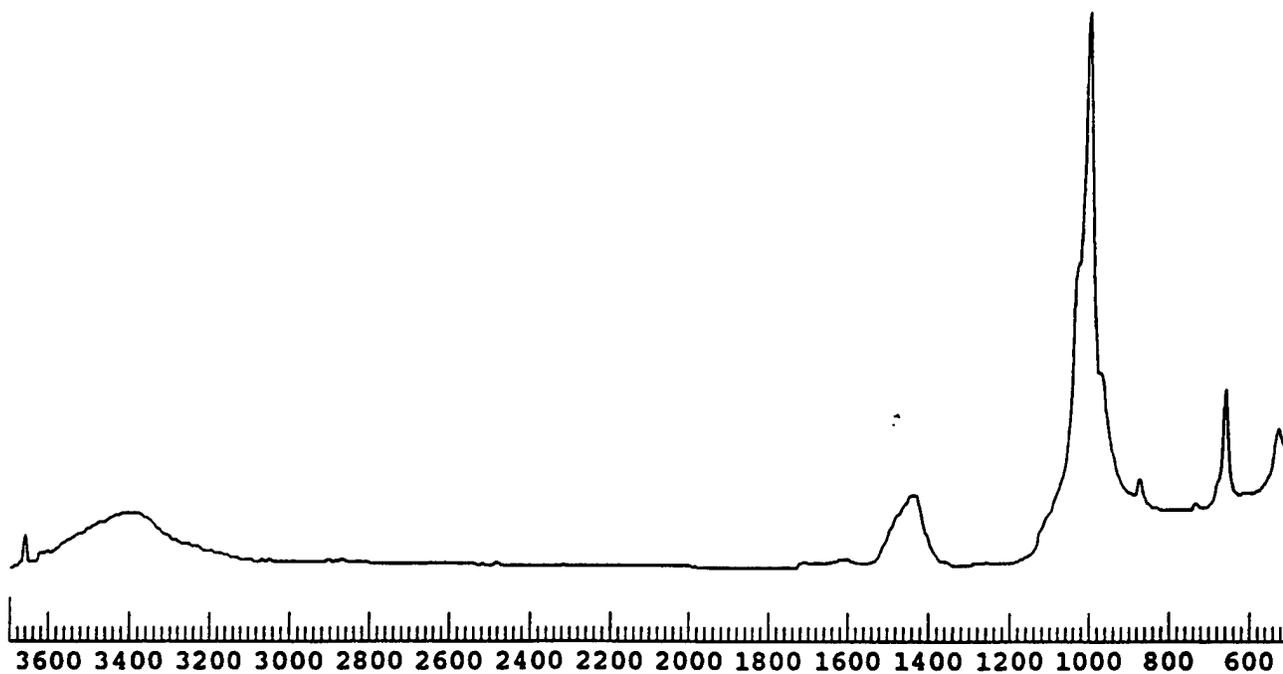
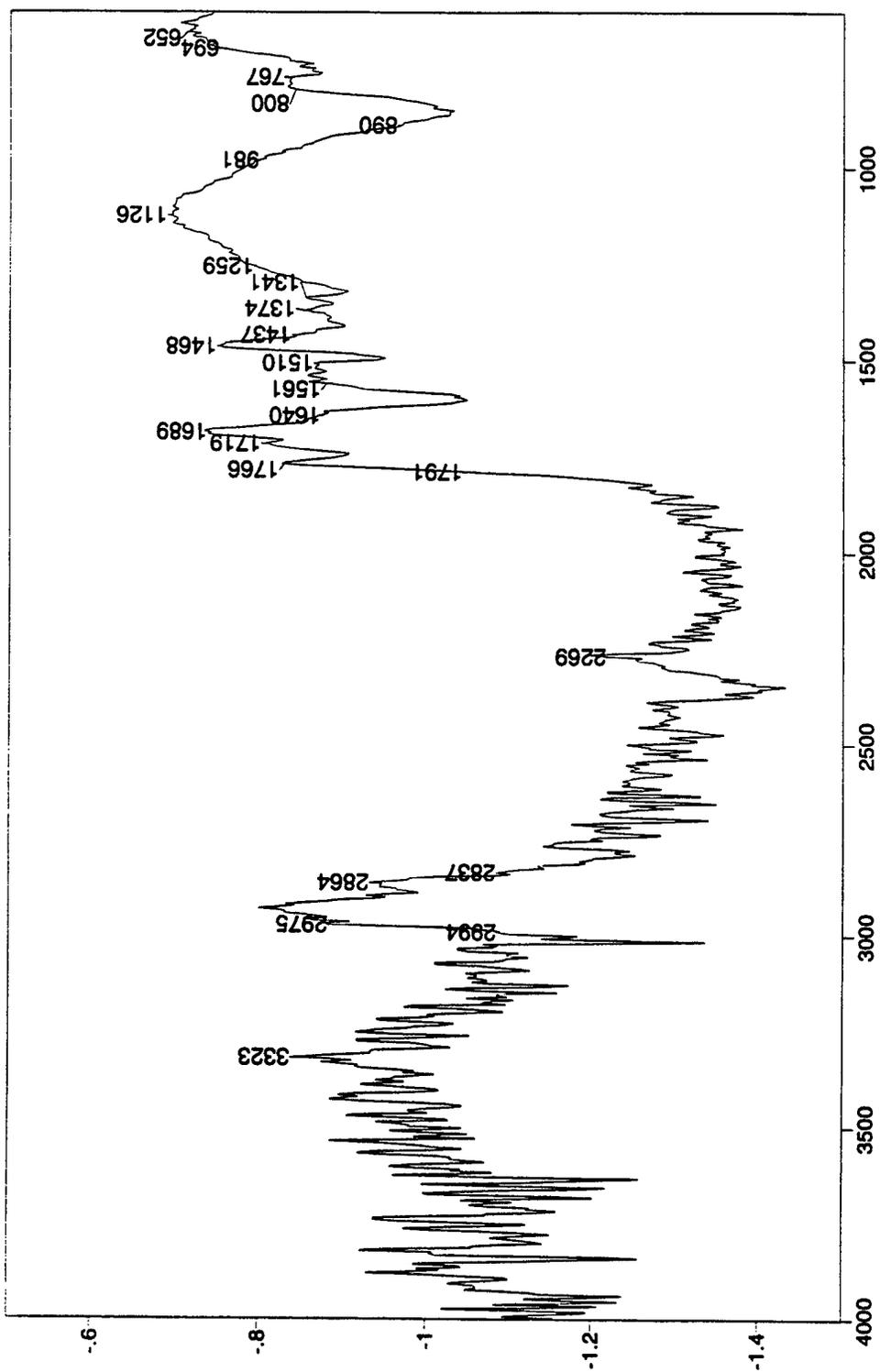


Figure 10. Sadtler Reference Spectrum of (a) Silica and (b) Magnesium Silicate.



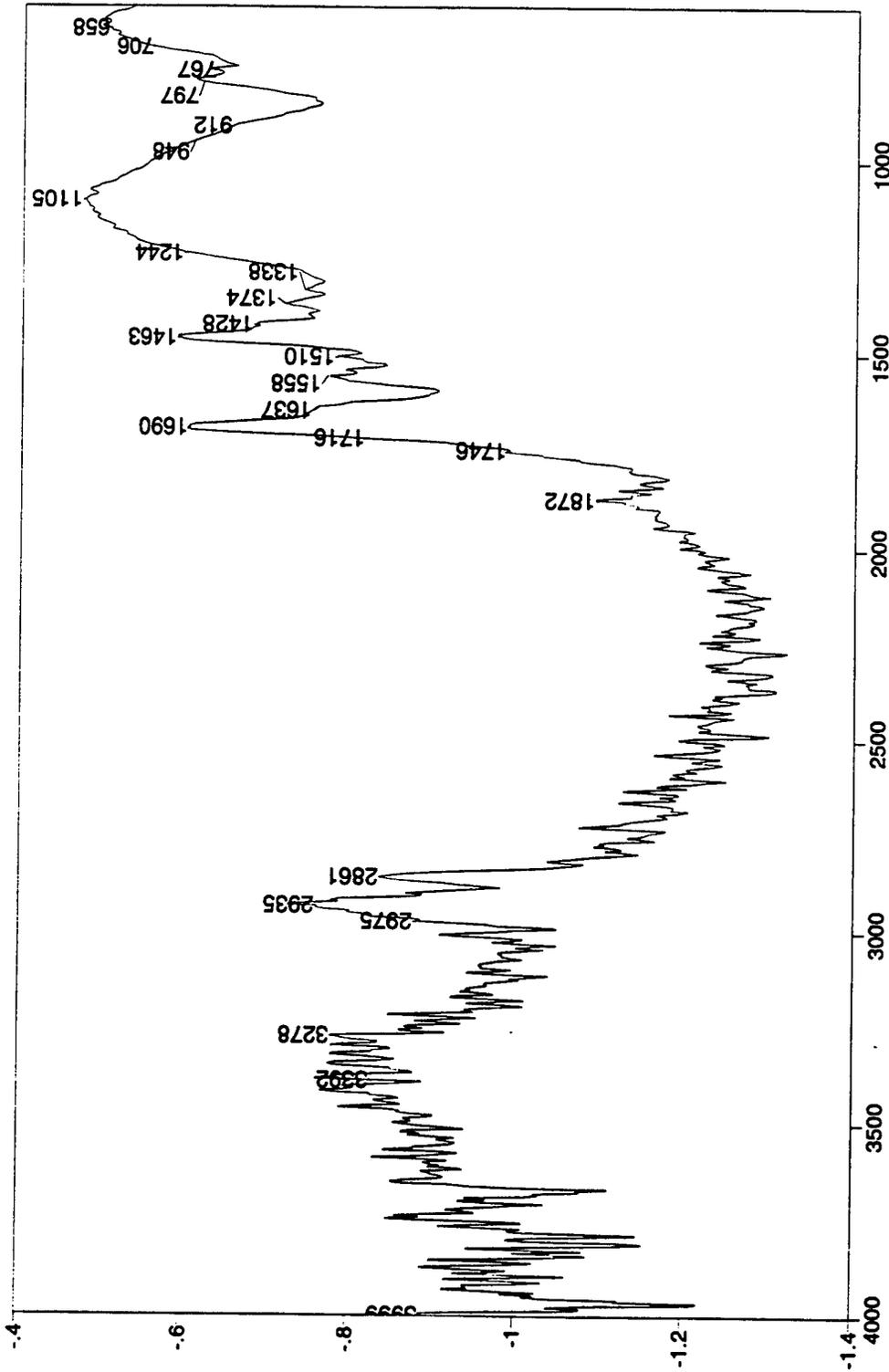
Paged Y-Zoom CURSOR
Res= 8cm-1

Absorbance / Wavenumber (cm-1)

File # 1 = 1WR2HE

E:\PAMPAS\WRPAINT\JAN9\cb2he = 2.862396\3.732300

Figure 11. PAS-IR Spectrum of the Virgin One-Pack Green Paint Sample.



Absorbance / Wavenumber (cm-1)

File # 1 = 1WR1HE

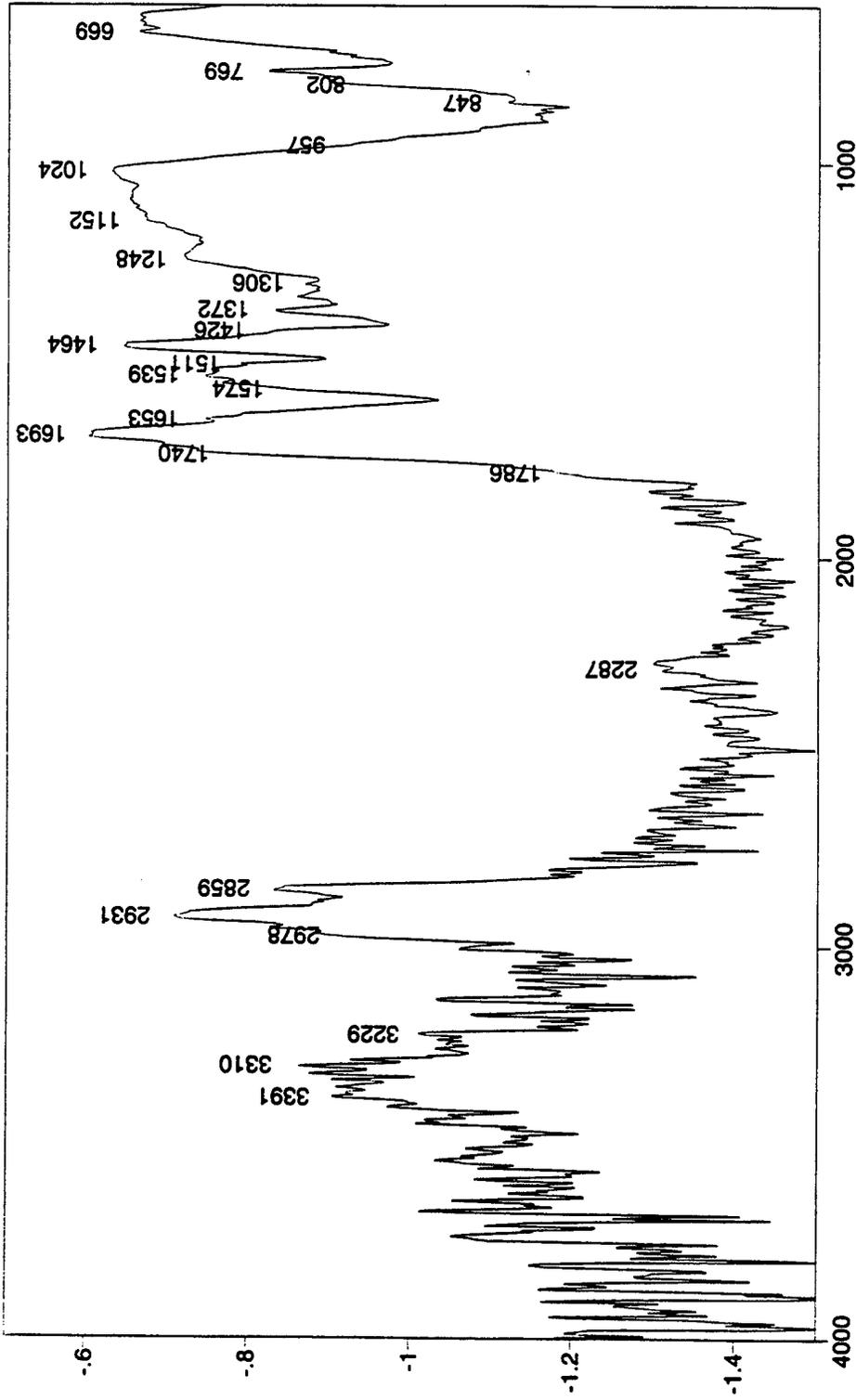
E:\PAMPAS\WRPAIN\JANG\cb2he = 2.862396\3.732300

Paged Y-Zoom CURSOR

Res= 8cm-1

Figure 12. PAS-IR Spectrum of the Plasma-Treated One-Pack Green Paint Sample.

1AWR2HE



Absorbance / Wavenumber (cm-1)

File # 1 = 1AWR2HE

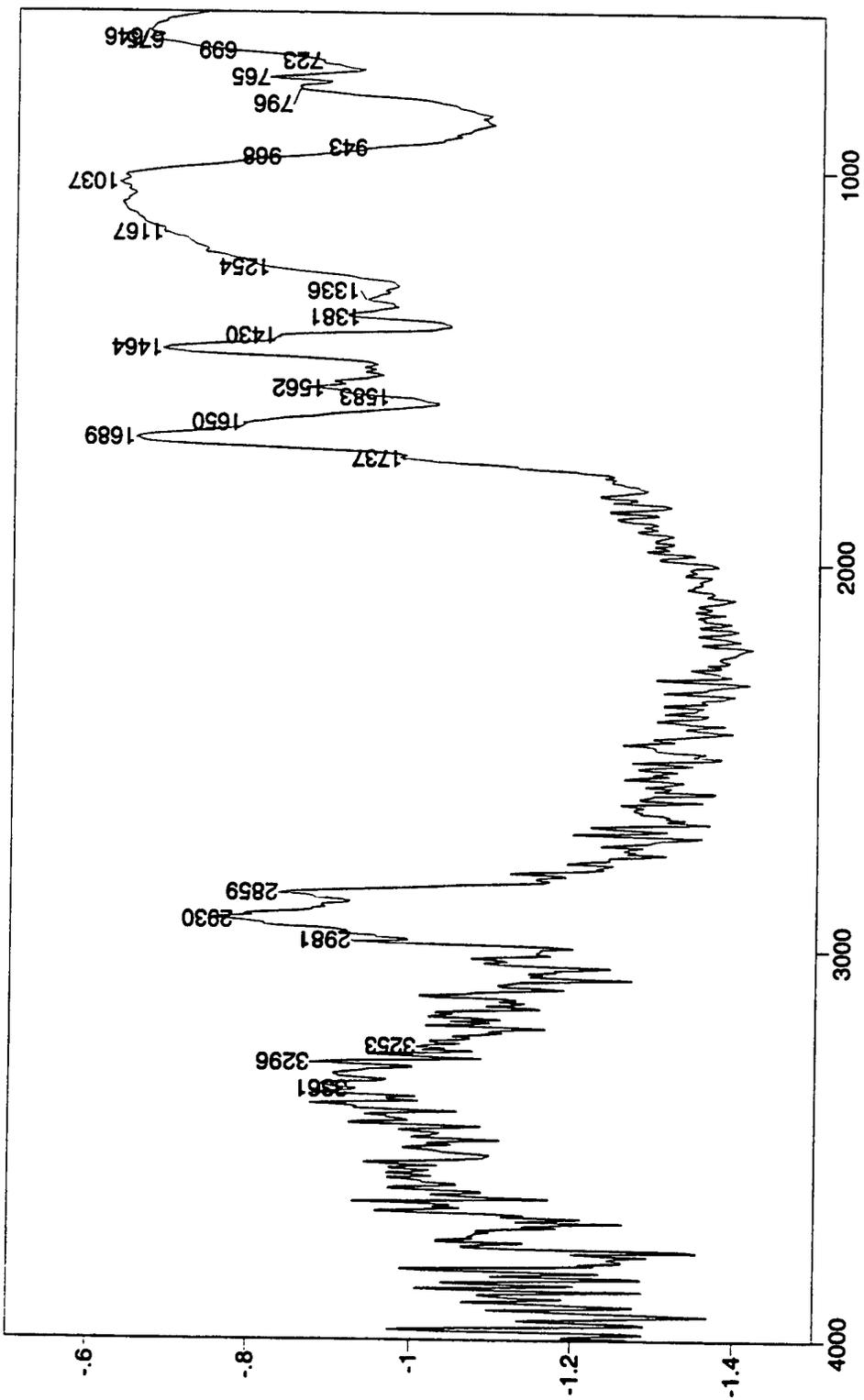
E:\PAMPAS\WRPAIN\TJAN9\cb1he

Y-Zoom CURSOR

Res= 8cm-1

Figure 13. PAS-IR Spectrum of the Untreated Two-Pack Green Paint Sample.

1AWR1HE



Absorbance / Wavenumber (cm-1)

File # 1 = 1AWR1HE

E:\PAMPAS\WRPAIN\TJAN9\cb2he = 2.8623996/3.732300

Y-Zoom CURSOR

Res= 8cm-1

Figure 14. PAS-IR Spectrum of the Plasma-Treated Two-Pack Green Paint Sample.

4.1.2.1 Virgin Experimental One- and Two-Pack Green Paint Samples. The spectra of the virgin green paints (compare Figures 11 and 13) appear very similar to each other with the exception that:

- The one-pack paint shows a distinct band at 1765 cm^{-1} not present in the two-pack paint. It is known that the one-pack paint contains an aromatic polyester and that absorptions near 1765 cm^{-1} are characteristic of aromatic groups on the carbonyl.
- The shape of the band in the silica region is different also, being broader in the spectra of the one-pack paint, reflecting the different morphology of the glass beads solids fill.

Compared to the virgin tan sample (Figure 5) the green paints have basically the same spectral features but with a few distinct differences:

- The carbonyl region is broader in the two green paints, probably reflecting differences between the polyurethane content of the tan moisture-cured and green water-reducible paints. Since the same company manufactures the water-reducible paints, they could contain some of the same, or similar, proprietary components. As mentioned previously, the one-pack paint also contains an aromatic ester, which is most likely the source of the 1765 cm^{-1} band. Nonetheless, all three paints have the isocyanurate ring at 1685 cm^{-1} as the most intense carbonyl peak.
- The aliphatic bands of the green paints have a stronger contribution from the terminal methyl group (2980 cm^{-1}). The C-H stretching in the green paints can arise from aliphatic groups of the polyol, which could have a terminal methyl group. The aliphatic bands are also broader, probably reflecting a greater variety of aliphatic groups.
- The green paints both show the 2270 cm^{-1} band, which is due to the unreacted isocyanate groups. The fact that isocyanate reacts readily with moisture in the air to form the urea, and that the PAS method probes the subsurface, is evidence that, upon curing a paint, a film forms that prevents evolution of isocyanate from the matrix. Thus, after the polyol and free hydroxyl functional

groups are reacted, a finite amount of the isocyanate monomer remains trapped. It is interesting that no monomer remains in the tan urea paint. It may be that the level of cross-linking achieved is not sufficient to form a sufficiently tight “skin” to retain the monomer.

4.1.2.2 Plasma-Heat-Treated Experimental Green Water-Reducible Paint Samples. Both the one- and two-pack experimental green paint samples were much more resistant to the plasma than the standard tan sample. Unlike the tan samples, for which most of the organic functional groups were eliminated, except for the isocyanurate and silica bands, the spectra of the green paint samples are only slightly modified. As opposed to the treated tan samples, spectra of the green samples remain rich in absorbance bands.

- Upon plasma treatment, the 1765 cm^{-1} polyester band of the one-pack green paint is eliminated. Attack at the ester group is not surprising, since esters are quite reactive and used frequently as intermediates in synthetic chemistry. The carbonyl bands of the one- and two-pack paints, although quite different for the virgin samples, are virtually identical after plasma treatment. The carbonyl absorbance at the low-frequency side, due to urea, remains after plasma treatment in both green paints. The absorbance in the $1720\text{--}1740\text{ cm}^{-1}$ region due to the polyurethane seems to be reduced. It is somewhat surprising that the urea is resistant to the plasma and that the polyurethane is reduced. In contrast, in the tan samples, the urea band was almost eliminated by plasma treatment. This is further addressed in section 4.2.5, Pyrolyzed Samples.
- The amide II band near 1550 cm^{-1} is reduced in the green paint samples but not eliminated as in the tan paint samples. In general, the bands below 1700 cm^{-1} do not return to baseline in the treated green samples, as was the case for the treated tan samples. This is consistent with the continued presence of the urea, as well as some polyurethane, both of which would also yield an amide II band.
- The diisocyanate monomer at 2265 cm^{-1} is eliminated in both green samples with plasma treatment.

In summary, the PAS spectra, which probes predominantly the subsurface of the green polyurethane/polyurea paints, show that the virgin green paints appear to contain a greater variety of organic species than the tan paint, as evidenced by broader carbonyl and aliphatic species. The green paints were both much more resistant to the plasma treatment than was the tan paint sample. In the green paint samples, the urea and polyurethane remain, as evidenced by the carbonyl and amide II bands; whereas in the tan paints, primarily only the inorganic species and isocyanurate remained. The aliphatic bands were still evident in the tan samples but were significantly reduced. The aliphatic bands in the green paints were only mildly affected, if at all.

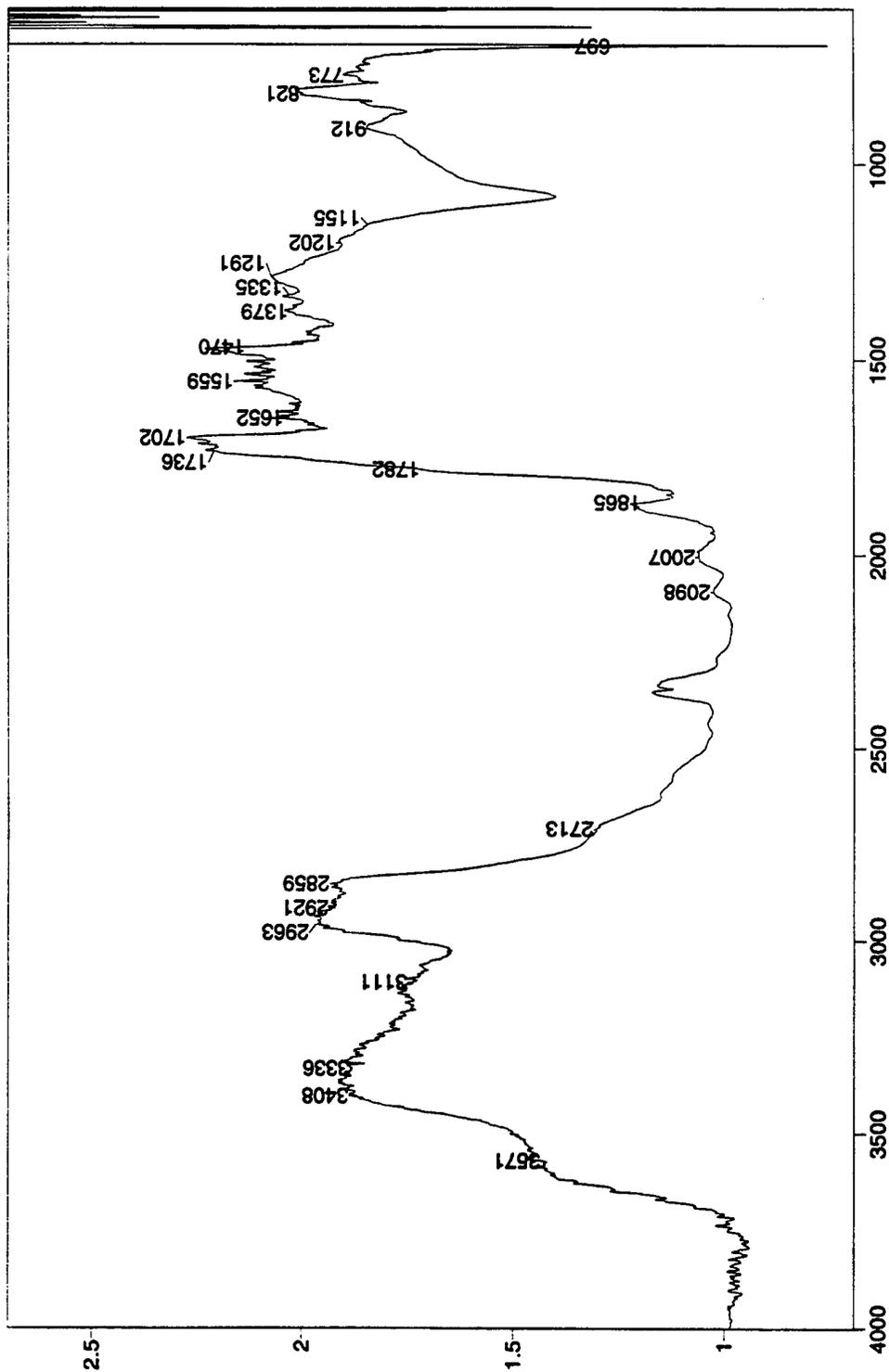
4.2 Reflectance Spectra. The reflectance spectra complement the PAS spectra in that the high-frequency region (particularly above 3000 cm^{-1}) has a much improved S/N ratio in the former. Thus, bands due to H bonds of O-H and N-H stretch modes are possible to analyze. Also, the reflectance method samples primarily the top $10\ \mu$ or less of the surface of the material, as opposed to the deeper-probing PAS method. Thus, differences between the two spectra can help elucidate surface vs. bulk phenomena, important in paint film formation and plasma-based paint removal.

Unfortunately, at frequencies below 2000 cm^{-1} , bands appear to saturate, particularly in the spectra of the virgin samples, which are designed to be very nonglossy and are therefore very different from the highly reflective aluminum surface used as the background. To avoid saturation, the absorbance range is ideally maintained below one absorbance unit. In most of the virgin samples, the range is 1.0–1.5 units. The large difference in reflectivity also accounts for the offset from zero in absorbance units. Also, greatly sloping baselines below 2000 cm^{-1} render it difficult to do quantitative work with this method using these samples. Baselines are the most distorted for treated samples, for which the surface becomes less specular and more irregular; increased exposure of the particulate solids fill material may add to the distortion. For these reasons, the method is best suited for semiquantitative work in which relative differences between samples are obtained. The method does offer the advantage of being able to adjust an aperture to focus down to spots on the order of $10\ \mu$. Also, important for this application, reflection enables paint spectra to be obtained which are too opaque to be analyzed by transmission spectroscopy.

4.2.1 Standard One-Pack Moisture-Cured Tan Paint Samples. Reflectance spectra of the virgin tan one-pack paint are shown in Figure 15, while those of the sample heated in vacuum (red sample) and the plasma-treated (grey sample) are shown in Figures 16 and 17, respectively.

At first glance, the reflectance spectra of the virgin samples appear very different from those from the PAS method (Figures 5–7), but most of the differences, particularly below 2000 cm^{-1} can probably be ascribed to the fact that bands in the reflectance spectrum are saturated and do not return to baseline. In the PAS and reflectance spectra of the heat-treated sample, the spectra appear more similar, with bands due to isocyanurate (1700 cm^{-1} and 1470 cm^{-1}) and urea (1650 cm^{-1}) being dominant. It is interesting that the silica band is more dominant in the PAS spectrum. It may be that the distribution of the silica in the bulk is greater, e.g., if the silica settled upon curing and the polymer fraction rose to the surface. There could also be a difference in the sensitivity of the two methods to silica. Both methods depend on the absorption coefficient of the material, but the PAS method also depends on the thermal conductivity of the sample. The thermal conductivity to amorphous silica tends to be 1–2 orders of magnitude greater for silica than for organic polymers (Touloukian et al. 1970).

The most striking differences between the PAS and reflectance spectra are in the bands above 3000 cm^{-1} , especially those that arise from NH groups (of urea or polyurethane) or NH_2 groups (from amines). In the PAS spectra, the NH/ NH_2 signals are just barely above the noise level. However, in the reflectance spectra, they are dominant features, so that the effect of heat and plasma treatment can be assessed. From the reflectance spectra, Figure 16, it is seen that the heat treatment alone results in reductions of the NH/ NH_2 signal. The urea (1650 cm^{-1}) and amide (1575 cm^{-1}) bands also appear to be reduced relative to the $1700/1475\text{ cm}^{-1}$ bands of the isocyanurate, but not to the same extent as NH/ NH_2 bands. These observations suggest that elimination of amines might be the primary reason for a much less intense NH signal in the treated samples, since amines do not contribute to the urea/amide bands that are not greatly affected. Thus, it seems as though some urea is removed but that the reduction of the NH/ NH_2 signal is probably also due to elimination of amines. An enrichment of the amine at the surface of the virgin sample is feasible, since it is formed from reaction of the isocyanate with moisture in the air and, as a monomer, would tend to reside at the surface in a



Absorbance / Wavenumber (cm-1)

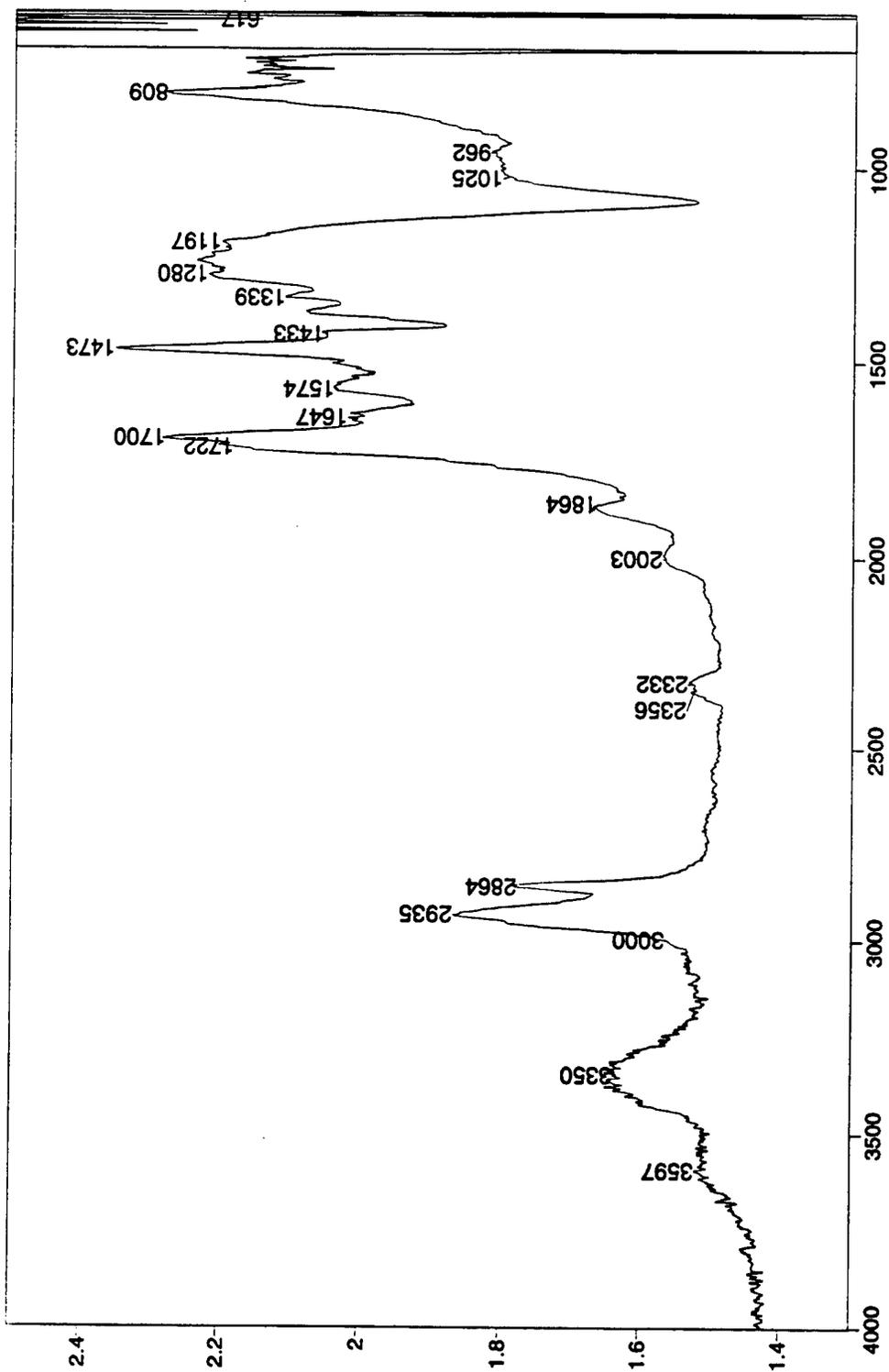
File # 1 = TAN1

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Paged Y-Zoom CURSOR

Res= 4cm-1

Figure 15. Reflectance IR Spectrum of the Virgin Two-Pack Green Paint.



Absorbance / Wavenumber (cm-1)

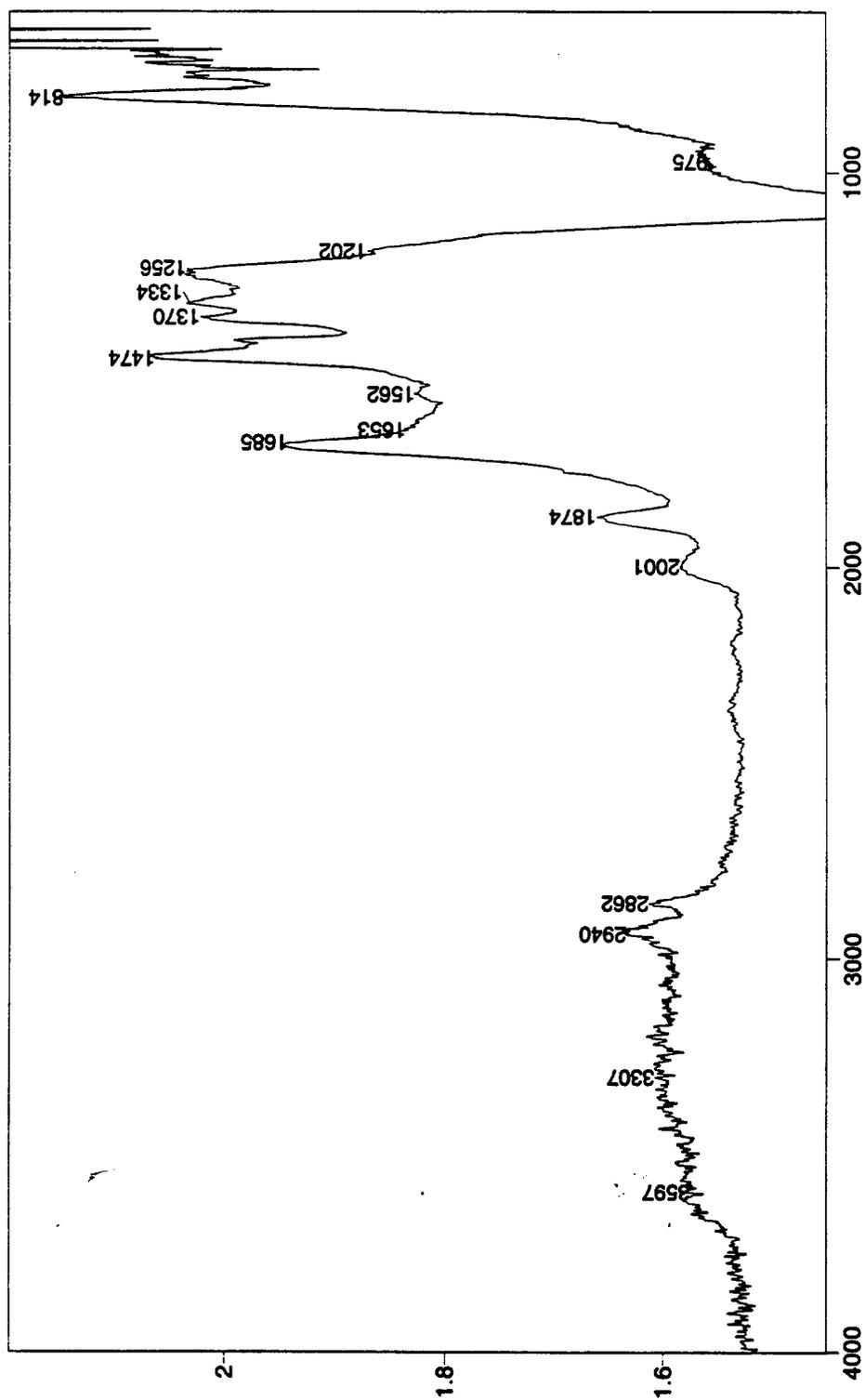
File # 1 = DKRED1

E:\PAM\REFLECTTAN\19MAR\dkred1 0.095978\0.123291

Paged Y-Zoom CURSOR

Res= 4cm-1

Figure 16. Reflectance IR Spectrum of the Heat-Treated One-Pack Tan Paint.



Y-Zoom CURSOR
Res= 4cm-1

Absorbance / Wavenumber (cm-1)

File # 3 = PLS1

E:\PAM\REFLECTAN\20MAR\pls1 = 0.120697\0.139160

Figure 17. Reflectance IR Spectrum of the Plasma-Treated One-Pack Tan Paint.

polymeric system. But, as mentioned previously, conclusive interpretation of bands below 2000 cm^{-1} is hampered by the fact that they are saturated in the virgin material, so that changes in the treated samples due to surface morphology alterations, rather than chemical changes, are difficult to deconvolve.

The great reduction of the NH/NH_2 bands with heating is definitive however. Another possible explanation could be that the urea groups undergo further cross-linking to form a mono- or di-substituted urea. In the latter case, the isocyanate could originate from the isocyanurate ring breakup, which would lead to less intense 1700 and 1475 cm^{-1} bands. In fact, the reverse occurs—the isocyanurate bands grow in relative intensity. Also, the amide band would be expected to diminish relative to the urea band, as the N-H groups of the urea were eliminated, and this is also not observed.

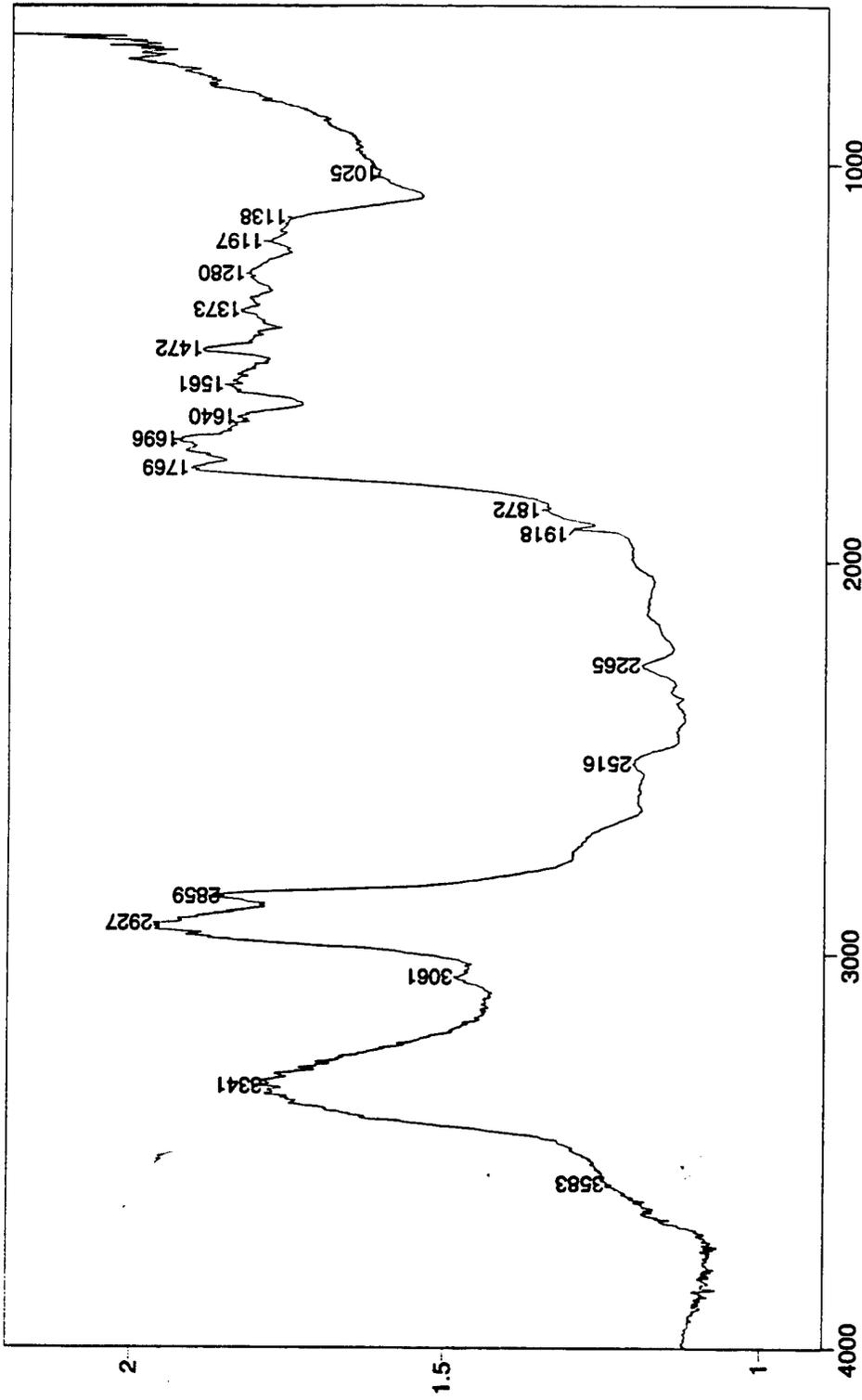
The carbonyl peak of the tan untreated sample is at 1700 cm^{-1} in both the PAS and reflectance spectra, but there is a high-frequency shoulder extending to 1780 cm^{-1} in the reflectance spectra. This shoulder is eliminated upon heat treatment and may be due to carbonyl vibrations of proprietary monomeric components, such as fatty acids derivatives, ethers, or polyesters. The fact that they are observed in the reflectance spectra (i.e., where monomers could align at the surface) and are readily eliminated by the heat treatment, support this. The net result is that the PAS and reflectance spectra of the heat-treated samples have bands at similar frequencies in the $1730\text{--}1375\text{ cm}^{-1}$ region.

The reflectance spectrum of the plasma-treated sample (Figure 17) shows that the aliphatic groups are very much reduced at the surface and that the dominant species remaining are the isocyanurate and silica species. The NH/NH_2 groups, dominant in the virgin sample, are almost eliminated in the spectra of the plasma-treated sample. Whereas the baseline in the PAS spectrum was flat, in the reflectance spectrum it is very curved, particularly from 2000 cm^{-1} to 1200 cm^{-1} . A tailing of the carbonyl peak the 1650 cm^{-1} and a slight absorbance at 1562 cm^{-1} suggest that only a minor amount of urea is still present. Bands at 1370 , 1334 , and 1256 cm^{-1} superimposed on the broader silica absorbance also indicate that some organic material remains.

In summary, the reflectance spectra of the tan one-pack paints, particularly bands above 3000 cm^{-1} , indicate that heat treatment results in loss of NH/NH_2 groups, probably from amines that reside on the surface and, to a lesser extent, urea groups. Plasma-treatment of the samples eliminates most, but not all, of the organic material. As in the PAS spectra of the plasma-treated samples, the dominant bands are due to silica and the isocyanurate ring. The reflectance spectra show that more aliphatic material is removed at the surface than was removed in bulk, as determined by comparison with the PAS spectra.

4.2.2 Experimental One- and Two-Pack Water-Reducible Green Paints. The reflectance spectra of the one- and two-pack green paints, virgin and untreated, are shown in Figures 18–21. As was the case with the tan paint samples, the reflectance spectra of the virgin samples appear saturated, particularly below 2000 cm^{-1} . The reflectance spectra have some features similar to the PAS spectra. Both spectra exhibit the 1700 cm^{-1} and 1465 cm^{-1} hexamethylene isocyanurate, the 1640 cm^{-1} urea, and the amide centered at 1540 cm^{-1} . As was also true for the tan paint samples, the N-H stretching band is seen more clearly above the much lower noise level of the reflectance spectra. However, unlike the tan paints in which the N-H stretch and aliphatic bands are virtually eliminated by plasma treatment, the green paints only exhibit a modest reduction in these bands. This is consistent with the observation that the green samples appear relatively undisturbed by the plasma treatment. Also, as in the tan paint, the silica bands are more dominant in the PAS spectra. Both the reflectance (Figure 19) and PAS (Figure 11) spectra of the virgin one-pack paint show the high-frequency carbonyl at 1765 cm^{-1} , which is attributed to the aromatic carbonyl of the phthalate group of the prepolymer.

The virgin samples of the two green paints (Figures 18 and 20) are similar, but do show different levels of the urea bands (1640 cm^{-1} , 1540 cm^{-1}) relative to the isocyanurate bands (1700 cm^{-1} , 1465 cm^{-1}). The two-pack paint has a relatively lower urea absorbance than does the one-pack paint, suggesting that less of this species exists in the two-pack paint. This is reasonable for a formulation that forms urethane cross-links as well as urea. There is also more isocyanate monomer remaining in the two-component paint—not surprising considering the high degree of indexing in the formulation.



Y-Zoom CURSOR

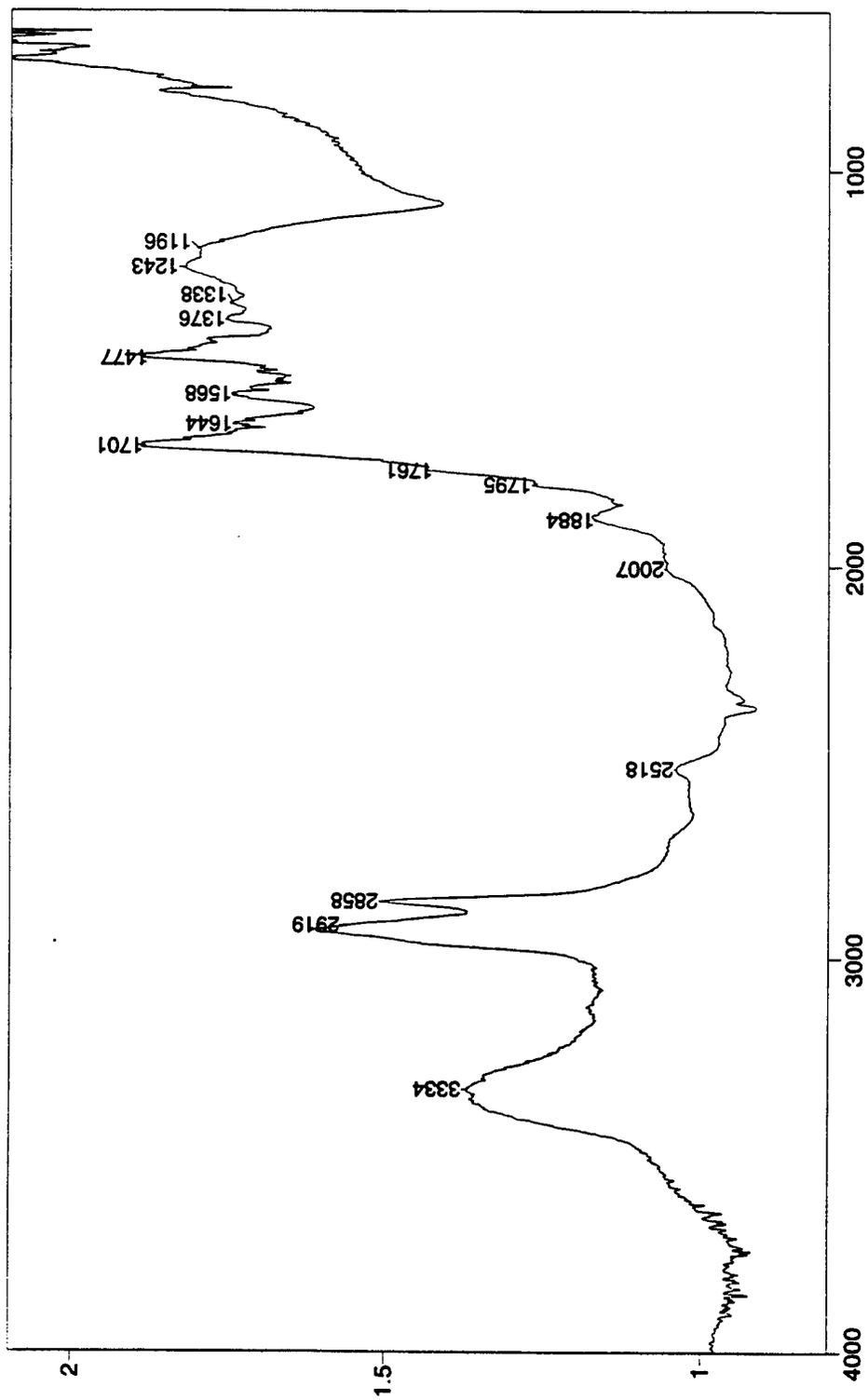
Res= 4cm-1

Absorbance / Wavenumber (cm-1)

File # 1 = 1WR2

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Figure 18. Reflectance IR Spectrum of the Virgin One-Pack Green Paint.

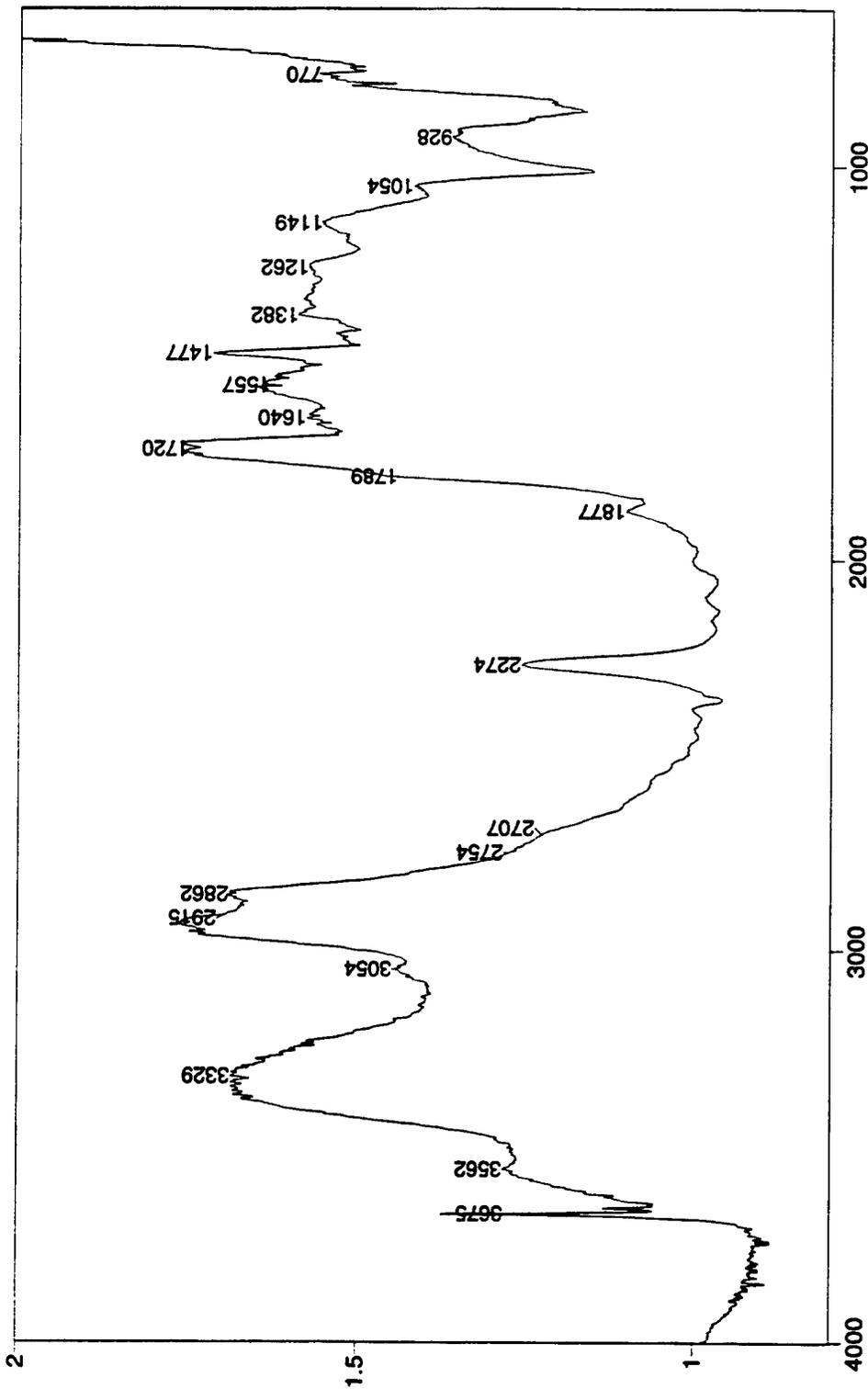


Absorbance / Wavenumber (cm-1)

File # 1 = 1WR1

E:\PAM\REFLECT\1WR1 16064, max = 0.232544/0.270081

Figure 19. Reflectance IR Spectrum of the Plasma-Treated One-Pack Green Paint.



Absorbance / Wavenumber (cm-1)

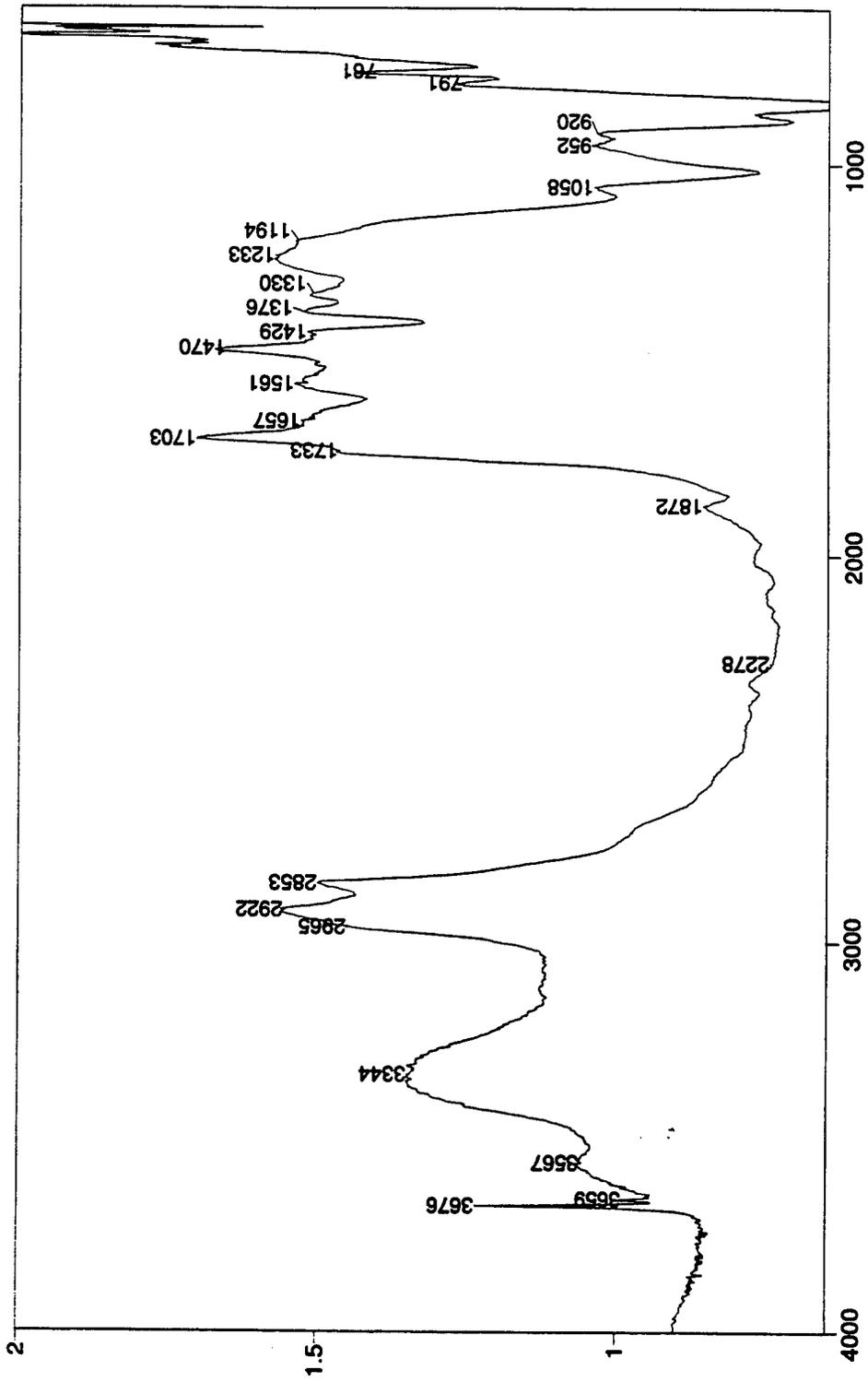
File # 2 = 1AWR2

E:\PAM\REFLECT\1AWR2 7814, max = 0.244751\0.244751

Y-Zoom CURSOR

Res= 4cm-1

Figure 20. Reflectance IR Spectrum of the Virgin Two-Pack Green Paint.



Y-Zoom CURSOR
Res= 4cm-1

File # 1 = 1AWR1

E:\PAM\reflect\1AWR1

Figure 21. Reflectance IR Spectrum of the Plasma-Treated Two-Pack Green Paint.

In both the reflectance and PAS spectra (Figures 11 and 13), the frequency of the urethane carbonyl leading edge shifts to a lower frequency (i.e., peak narrows) upon treatment (Figures 12 and 14 for PAS spectra), but this occurs to a greater extent in the one-pack paint that actually has a distinct peak at 1770 cm^{-1} in the untreated sample, which is not present after treatment. In the green paints, as well as in the tan paints, the silica band is much more dominant in the PAS spectrum.

The isocyanate monomer band at 2265 cm^{-1} is detected in the PAS spectra of both the one- and two-pack untreated green paints and appears at comparable levels. In the reflectance spectra, however, it is clear that there is significantly more unreacted HDI in the two-pack paint than in the one-pack paint. These observations need not be in disagreement: both paint samples may contain about the same level of HDI monomer in the bulk material and have different levels at the surface. It is interesting that the isocyanate monomer can remain relatively close to the surface (tens of microns) without reacting with atmospheric moisture. Moreover, no unreacted HDI was observed in the tan moisture-cured samples. The presence of HDI in both green paints may be a consequence of tighter cross-linking and skin formation, which may not occur in the tan samples.

In both green samples, plasma treatment eliminates the unreacted HDI. Whether this occurs through volatilization or further reaction is of interest for the potential application of plasmas to the study of improved paint structure/adhesion. At the plasma intensity/heat treatments used for these samples, the reflectance data (Figures 18 and 19) suggest that, in the standard one-component paint, there seems to be a net decrease in urea functional groups in the treated samples, as evidenced by the relative decrease in the urea and N-H bands. For the two-component water-reducible green paint, the urea band may actually increase (Figures 20 and 21), while the amide and N-H bands decrease. If real, an increased urea level would be consistent with the plasma-assisting reaction of the unreacted isocyanate with urea groups already present to form the disubstituted ureas. In this case, as the hydrogen is removed, the number of N-H bonds decrease as the biuret is formed and the amide II band diminishes. A Sadtler reference spectrum of a urea biuret—a tetramethyl analog of the hexamethyl groups that would exist in the paint—is shown in Figure 22. Note that since no N-H groups exist, there is no amide band at 1540 cm^{-1} .

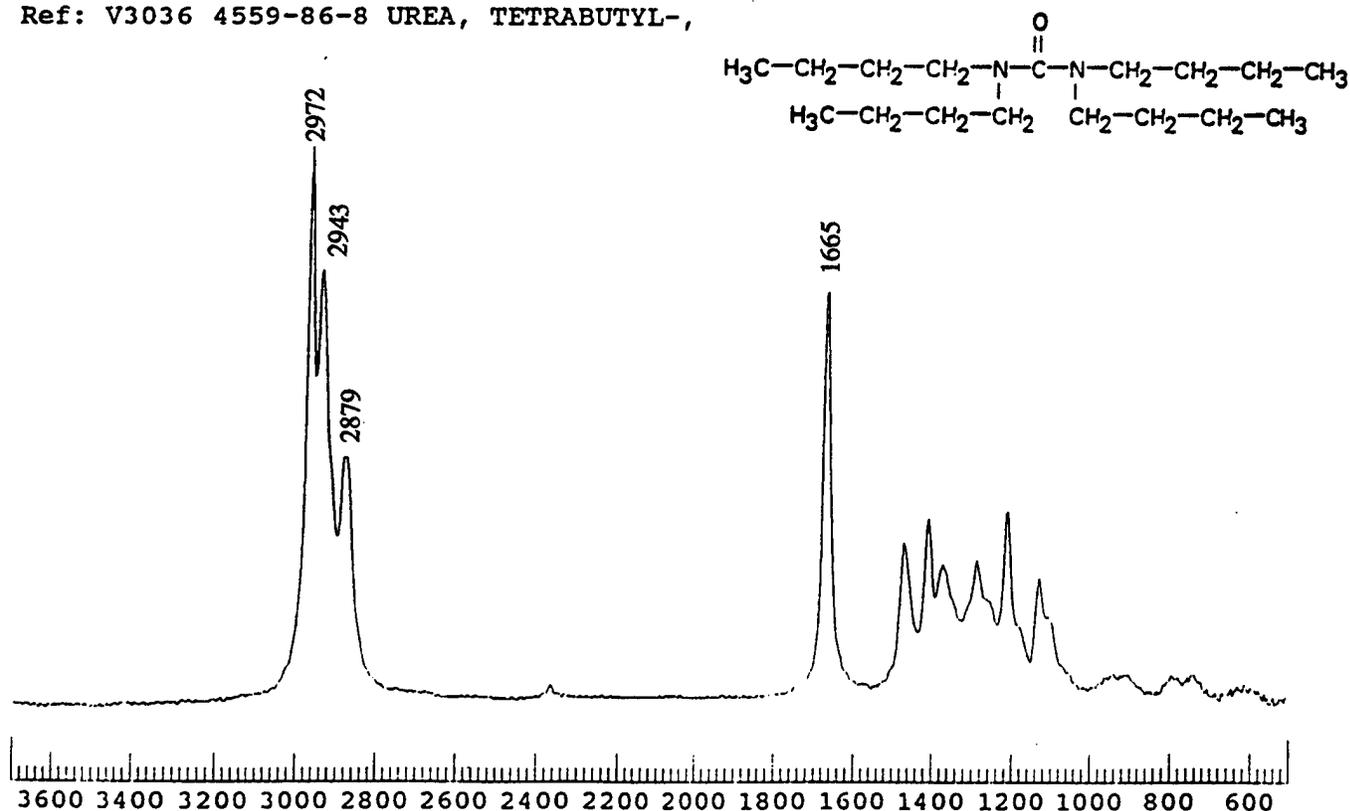
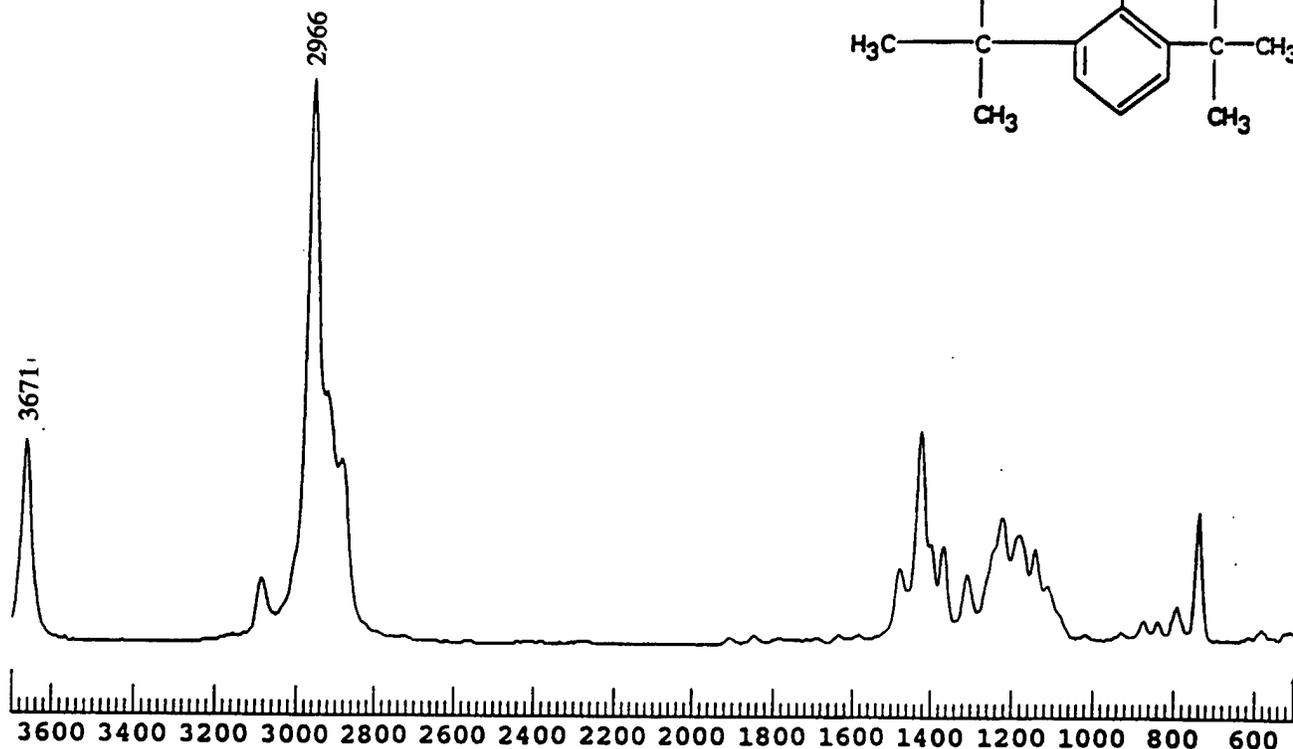
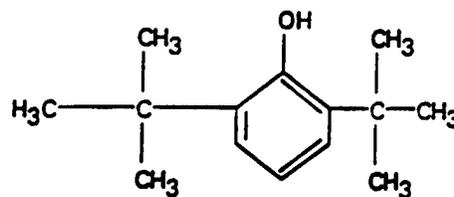


Figure 22. Sadtler Reference Spectrum of the Tetramethyl Urea Biuret.

Another interesting difference in the reflectance spectra of the green paints is that the two-pack sample has a very sharp, distinct band, probably due to free hydroxyl groups, at 3675 cm^{-1} . This is not found in the one-pack paints or in the PAS spectra of the bulk material. Free hydroxyl groups are usually only found in the gaseous state; otherwise, associations between hydroxyl groups occur. Nonetheless, the band is found in every reflectance spectrum of this material, including those obtained after plasma treatment. An exception in which the free hydroxyl band is present in condensed phases includes tertiary compounds in which the hydroxyl group is sterically hindered from hydrogen bonding interactions (Figure 23a). Also, talc (magnesium silicate) is known to be present in the two-pack paint, and a reference spectra of the chrysotile form $\text{Mg}_6(\text{Si}_4\text{O}_{10})(\text{OH})_8$ of magnesium silicate shows a band at 3680 cm^{-1} (Figure 23b). A variety of magnesium silicates are used as fillers. Also, the physical descriptions of some magnesium silicates in the Sadtler library have indicated that in practical use, phenols with tertiary carbons can be present as well, and they absorb in the 3675 cm^{-1} region. Note that the reference spectrum of the chrysotile form has bands at 1060 and 950 cm^{-1} ,

Ref: V6860 128-39-2 PHENOL, 2,6-DI-TERT-BUTYL-,



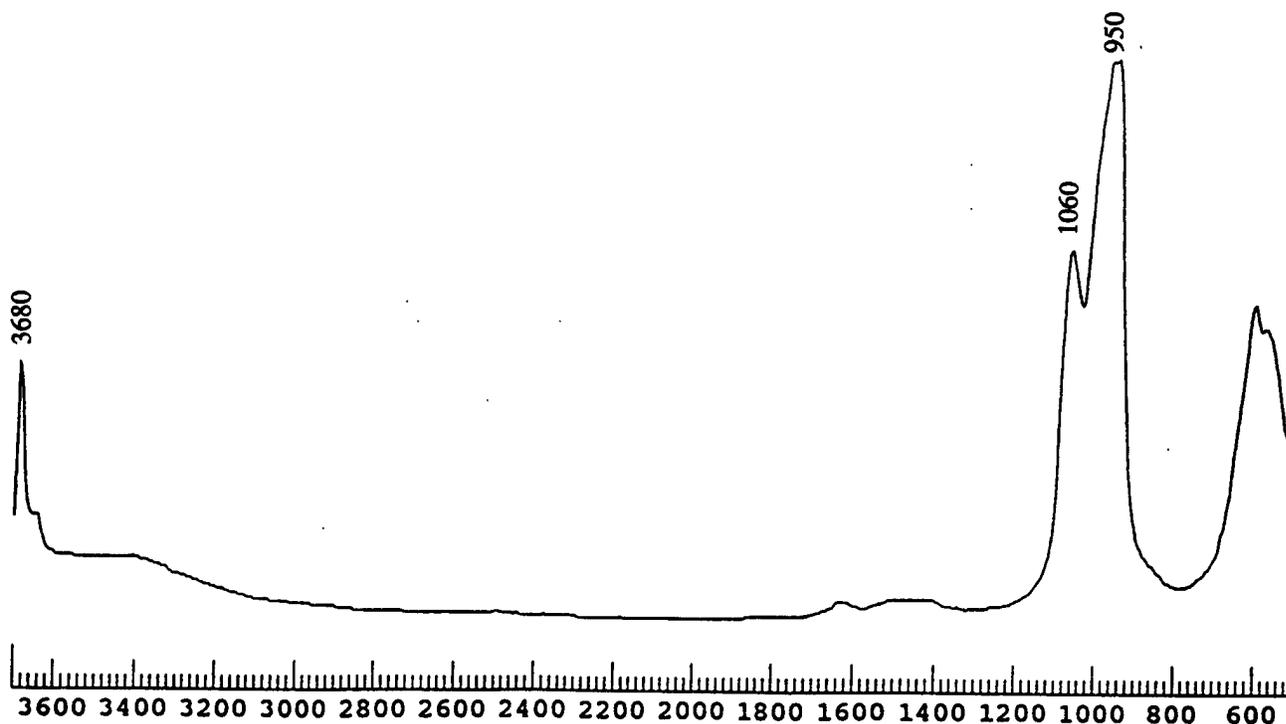
(a)

Figure 23. Sadtler Reference Spectra Containing Bands at 3675 cm⁻¹: (a) 2,6-di-tert-butyl Phenol and (b) Chrysotile, Hydrrous Magnesium Silicate, Mg₃(Si₄O₁₀)(OH)₂.

which are also seen in the two-pack green paint, before and after plasma treatment, but not the one-pack green paint at all. Silanols also have absorptions in this region (Bellamy 1975).

In summary, the reflectance spectra of the experimental one- and two-pack green water-reducible paints show that:

- Unlike the standard tan paints, in which the N-H stretch and aliphatic bands are virtually eliminated by plasma treatment, the green paints exhibit only a modest reduction. Visual inspection of the samples shows that the green samples appear relatively undisturbed by the plasma treatment.



(b)

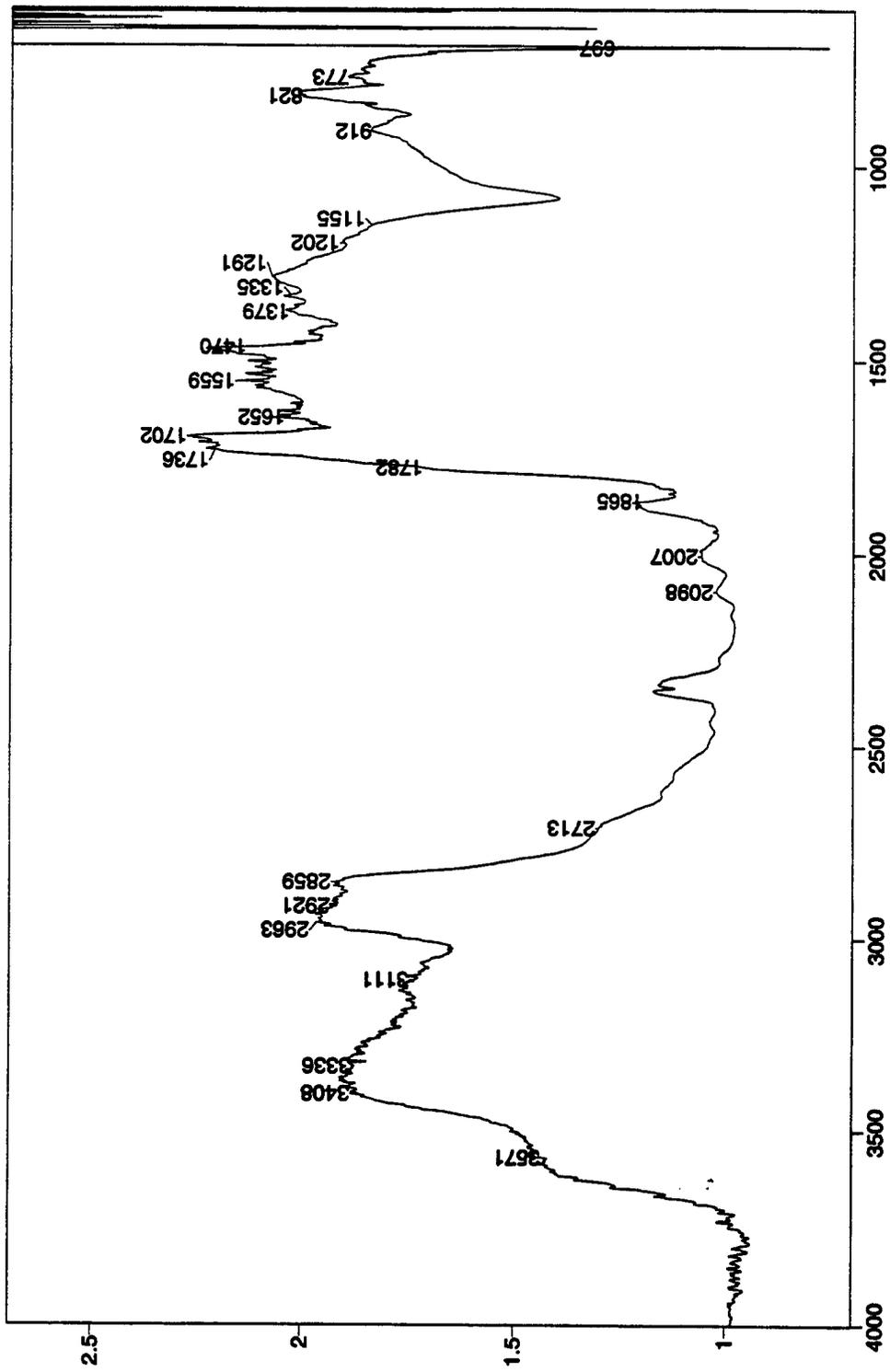
Figure 23. Sadtler Reference Spectra Containing Bands at 3675 cm^{-1} : (a) 2,6-di-tert-butyl Phenol and (b) Chrysotile, Hydrous Magnesium Silicate, $\text{Mg}_6(\text{Si}_4\text{O}_{10})(\text{OH})_8$ (continued).

- As in the tan paint, the silica bands are more dominant in the PAS spectra.
- Both the reflectance and PAS spectra of the green one-pack paint show the high-frequency carbonyl at 1765 cm^{-1} , which is attributed to a phthalate prepolymer. Both sampling methods show that this band is eliminated in the plasma-treated samples.
- The two-pack paint appears to have relatively less urea than does the one-pack paint, consistent with the fact that the former can form urethane cross-links. The two-pack paint also contains more isocyanate monomer, consistent with its high-isocyanate index.

- Upon plasma treatment, the one-pack, moisture-cured paint appears to lose isocyanate and urea groups. The spectra of the two-pack paint suggest that the isocyanate may cross-link further to form the biuret. Further confirmation is desired.
- The two-pack sample has a very sharp, distinct band, due to free hydroxyl groups, at 3675 cm^{-1} , which may be due to a sterically hindered organic hydroxyl-containing compound, or to magnesium silicate.

4.2.3 Mildly Heated Standard Tan One-Pack Water-Cured Paint Samples. During the first experiments to establish plasma parameters effective in paint removal, a series of samples were treated under milder temperature (150° C) and plasma conditions. These samples remained tan and were only slightly different from their original color. Although visually the samples were nearly identical, the reflectance method yielded spectral changes that were quite distinct. Figure 24 shows the spectra of the untreated and mildly heat/plasma treated samples. As in the reflectance spectra of the samples exposed to the stronger plasma treatment (Figures 15–17), the carbonyl band loses its high-frequency absorption above 1740 cm^{-1} , and the NH/NH_2 bands ($3300\text{--}3400\text{ cm}^{-1}$) decrease, although the latter effect is less with the mild plasma treatment. Most importantly though, in the spectra of the mildly treated samples, the urea and amide bands grow and even exceed the silica bands in intensity. The more intense urea and amide bands support the likelihood that under mild heat and plasma treatments more urea bonds form.

Since no unreacted isocyanate was detected in the tan paint samples, it may be that the isocyanurate ring opens to provide the isocyanate needed for urea formation. The simultaneous decrease in the ($3300\text{--}3400\text{ cm}^{-1}$) band and growth of the amide band can be best explained by removal of amine hydrogen and formation of urea. The alternative explanation for the decrease in the $3300\text{--}3400\text{ cm}^{-1}$ band would be removal of the free hydrogen in the urea linkage to form the disubstituted ureas. However, that would cause a decrease in the amide band and is inconsistent with observed growth of this band. Urea formation from amine groups is feasible, particularly since the experiment is run under vacuum and no water would be available for competing reactions with the isocyanate.



Absorbance / Wavenumber (cm-1)

File # 1 = TAN1

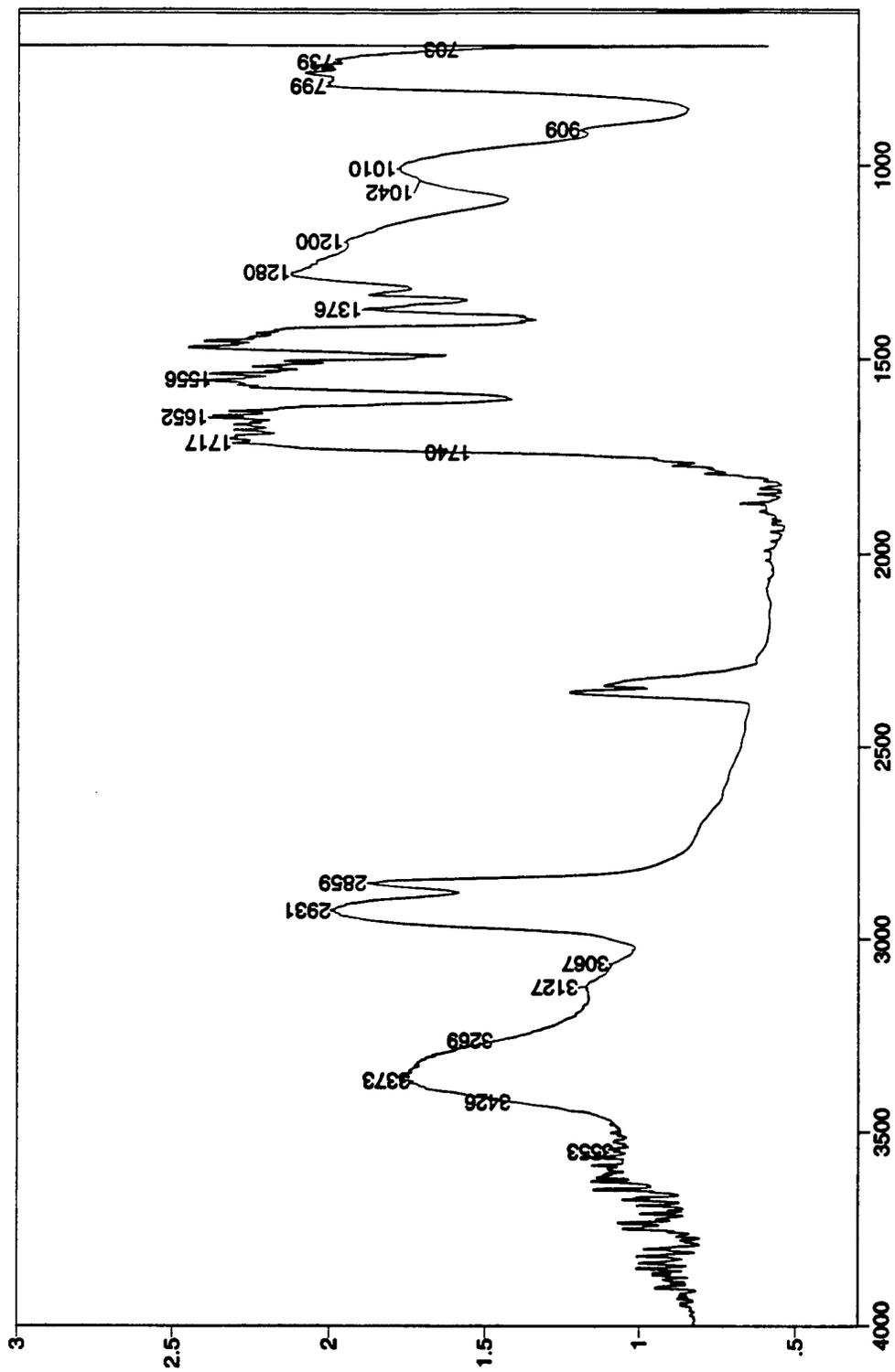
E:\PAM\REFLECTAN19\MAR\tan1 = 0.257263\0.257263

Paged Y-Zoom CURSOR

Res= 4cm-1

(a)

Figure 24. Reflectance IR Spectra of: (a) the Untreated, and (b) the Mildly Heat/Plasma-Treated Samples of the One-Pack Tan Paint.



Absorbance / Wavenumber (cm-1)

File # 1 = PLSMILD

E:\PAM\REFLECTTAN\19MAR\plsmild 0.617218\0.617218

(b)

Paged Y-Zoom CURSOR

Res= 4cm-1

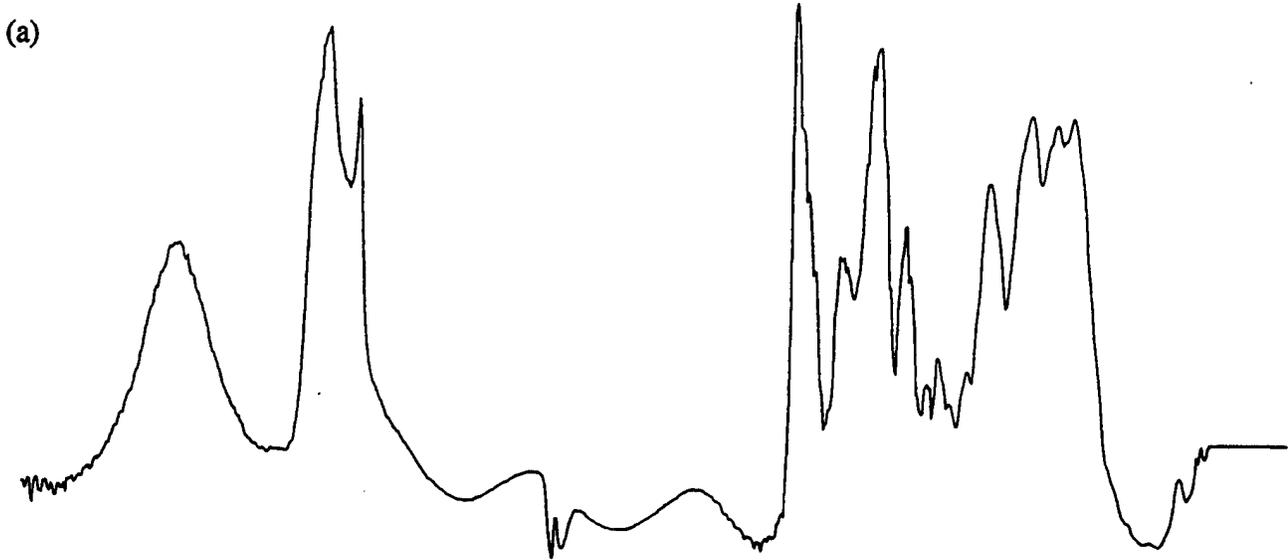
Figure 24. Reflectance IR Spectra of: (a) the Untreated, and (b) the Mildly Heat/Plasma-Treated Samples of the One-Pack Tan Paint (continued).

Heat treatment (150° C) alone gave a spectrum virtually identical to the untreated tan sample. Thus, if the conversion from amine to urea occurs as proposed, the mild plasma treatment is essential. Mild plasma treatment could have potential for improving properties that rely on thorough cross-linking, such as adhesion and impact, chemical-agent resistant coating (CARC), and corrosion resistance. As discussed previously, strong plasma treatment of the tan samples removes all the organic groups except some isocyanurate monomer; the inorganic silica remains also. Thus, with control of the intensity and duration of the plasma/heat treatment, it may be possible to increase the number of cross-links in the paint (mild plasma) or virtually eliminate the cross-links (and other organic matter) in the urea paint structure (intense plasma). Understanding the role of the isocyanurate monomer in this process is critical, since it appears that a significant amount (although not all, as evidenced by the relative intensity of its bands to that of silica) remains after intense plasma treatment, but some may break down under mild plasma treatment to provide the monomer for further urea formation.

4.2.4 Experimental Water-Reducible Two-Pack Paint Components. Attempting to make band assignments for the cured and plasma-treated paints is, as mentioned above, quite complex. In an effort to simplify the problem, the reflectance spectra of the individual paint components, as well as some extracts, of the two-pack green paint were analyzed. Component A is a complex mixture containing the polyol and pigments, and Component B contains the isocyanate. Moreover, Component A had settled for several weeks prior to opening and had partitioned into a somewhat transparent purple layer (less than 10% by volume) and a thick opaque layer containing the solids fill and comprising the bulk of the material. Some of the purple layer was removed and sampled by IR. An acetone extraction, prepared with an excess volume of paint with a much smaller amount of solvent, dried to a light lavender residue (i.e., not much purple pigment was extracted).

The reflectance spectrum of the shiny, intense purple sample that dried in the aluminum pan has the typical urethane band profile, which is due to the use of a urethane-polyol prepolymer to disperse the pigment (Figure 25a). The carbonyl at 1744 cm^{-1} is much sharper than that observed in the cured paint samples, suggesting a single urethane structure in the prepolymer. A reference spectrum of a commercially available polyol-urethane prepolymer is also provided (Figure 25b). Although band

Unk: PURBUB.ISP E:\PAM\TWOPACK/purbub



Ref: OL612 SPENKEL P49-75S*POLYOL ADDUCT TYPE URETHANE PREPOLYMER

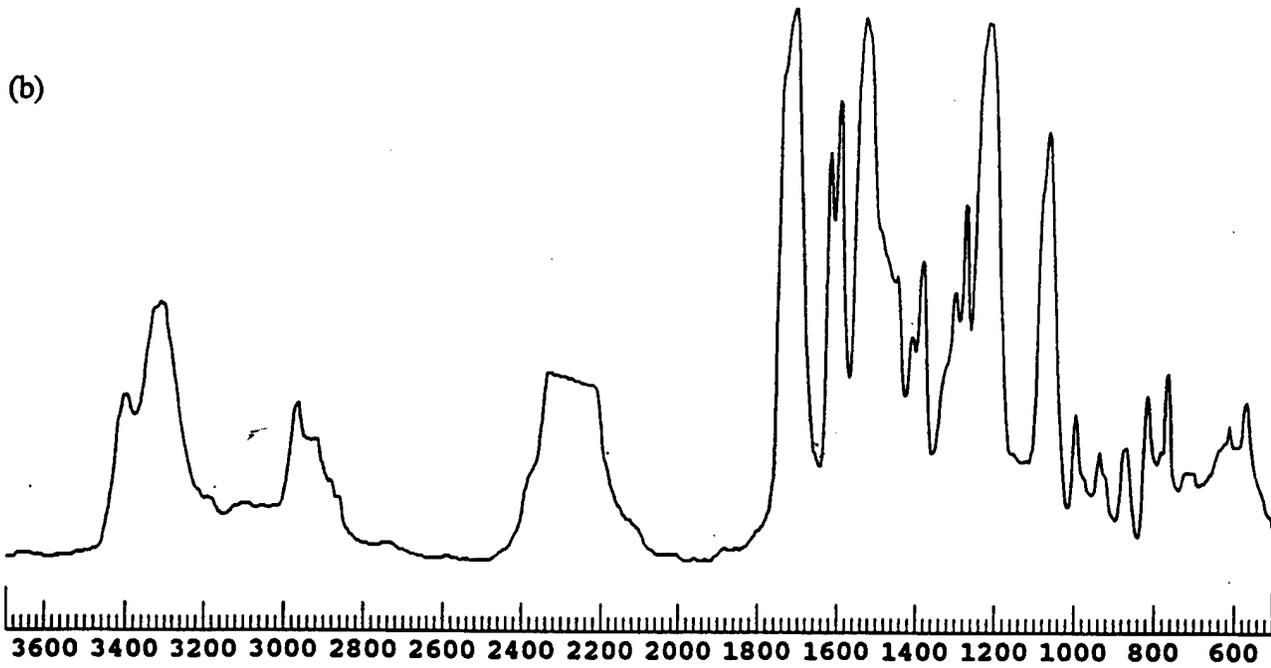
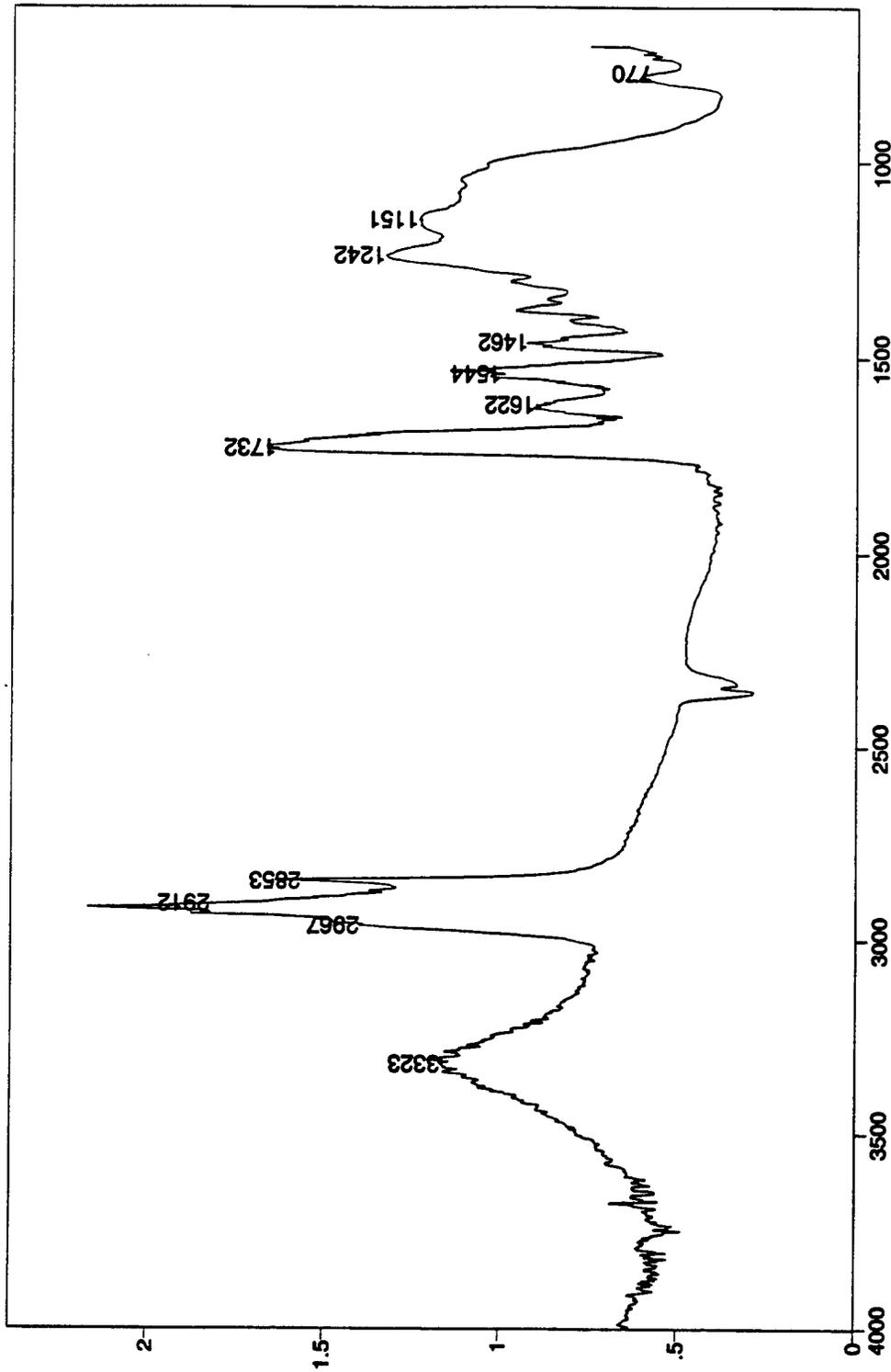


Figure 25. (a) Spectrum of the Purple Layer of Component A of the Two-Pack Paint, After Drying, and (b) Sadtler Reference Spectrum of a Polyol/Polyurethane Prepolymer.

intensities are different, the frequencies of the major bands match well. The exact polyol used is key to a successful formulation, and structures vary with application; thus, an exact library match was not expected. Polyol structures are almost always proprietary, so they are not typically available with the reference spectrum. Some sort of polymerization appears to occur: the original purple sample is miscible in water but dries to a film that does not redissolve in water (it does in acetone).

A reflectance spectrum of a sample of component A after the two layers were mixed and allowed to dry was also obtained (Figure 26). The silica bands are not as dominant in this spectrum as in a sample of the formulation cured with isocyanate. Since component A alone does not cross-link and takes a comparatively long time to dry, the silica groups have more time to settle. Organic material, especially monomers rise to the top. In fact, this paint dried to a maroon color due to the purple pigment separating prior to drying. This sample also has a typical polyurethane spectrum, although judging by the differences in relative intensity between the $1730/40\text{ cm}^{-1}$ and 1545 cm^{-1} bands, it is probably a different polyurethane polyol. Unlike the spectra of the cured paint sample, the spectra of these individual components show distinct bands with clear separation (i.e., more closely resembling a single component urethane spectrum). The broad bands obtained from the cured paint samples, especially in the region between $1000\text{--}1800\text{ cm}^{-1}$, may in part reflect the complexity of the final composition. However, samples from component A were much more glossy and reflective than was the cured paint sample. Thus, the abnormally high sloping baseline is probably also an artifact of the sample surface morphology as well.

It is interesting that the two-component, water-reducible paint contains a polyurethane prepolymer, as does the one-component, water-reducible formulation. Both these paints have similar properties, and they are made by the same company. Thus, it may be that the polyurethane prepolymer influences the paints' characteristics as much as the actual polymerization mechanism (polyurea formation for one-component paints; polyurethane and polyurea for two-component paints) or the morphology of the fill (the formulations with similar reaction to the plasma had different solids fill).



Absorbance / Wavenumber (cm-1)

File # 1 = GPMIX3

E:\PAMTWOPACK\gpmix3 942, max = 0.257111\0.280304

Res= 4cm-1

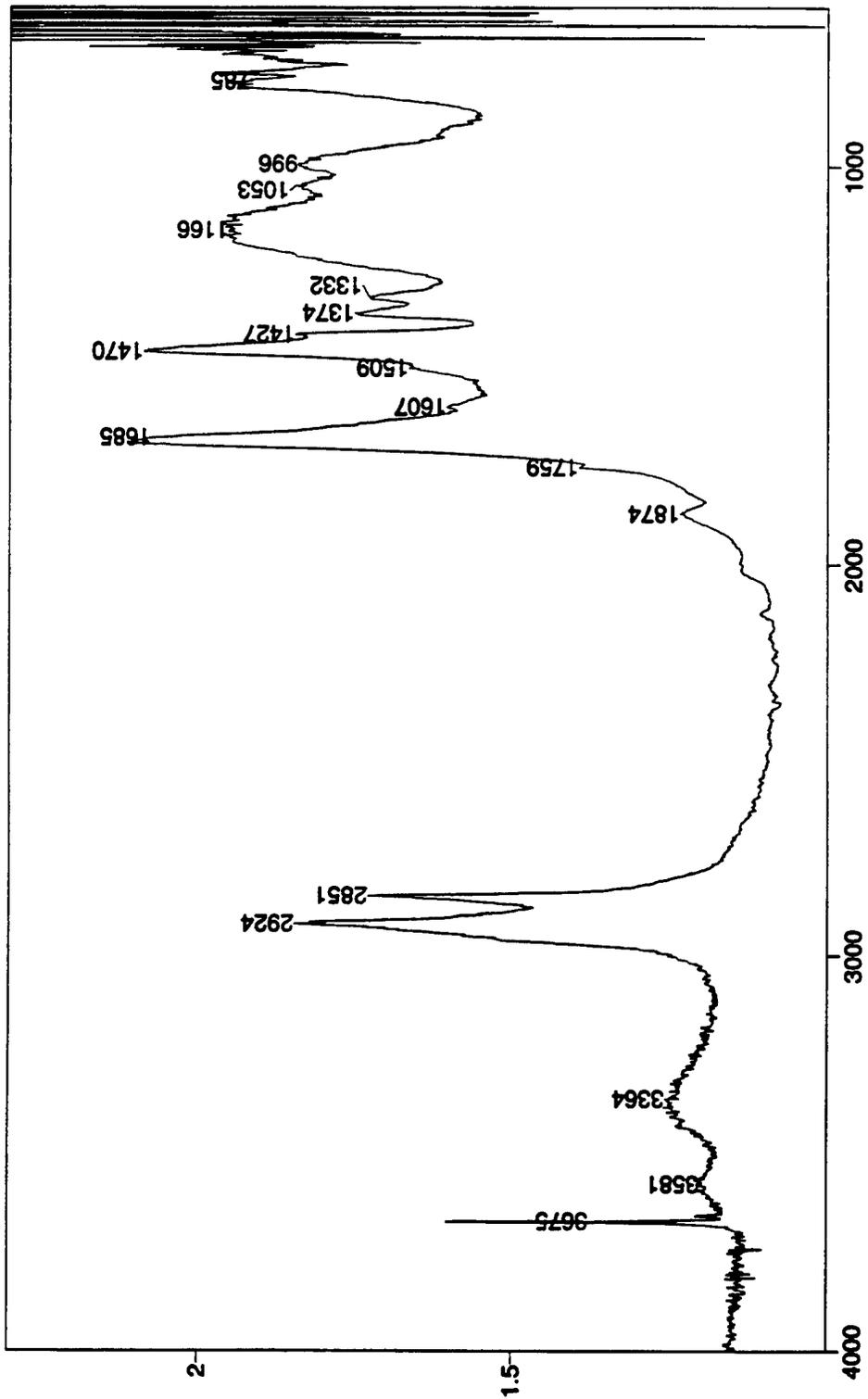
purple & gm layers mixed; no isocyanate added; dries maroon; very thin layer sample

Figure 26. Reflectance Spectrum of Component A of the Two-Pack Paint After It Was Thoroughly Mixed and Allowed to Dry.

4.2.5 Pyrolyzed Samples. The virgin and plasma/heat-treated two-component water-reducible green paint samples were heat-treated at approximately 800° C for 20 s in helium. The tan paint moisture-cured samples exposed to the same treatment appear virtually disintegrated. Because only a minute amount of material remained and because it was so ashen, the reflectance spectrum of the tan paint pyrolysis residue was not obtained. Both virgin and plasma-treated one-pack and two-pack water-reducible paint samples were particularly inert, and appeared visually intact, with no color change, after the pyrolysis treatment. IR spectra of the residue for each sample were virtually identical; that for the plasma-treated sample is presented in Figure 27. The spectrum shows that the amide and urea bands are much diminished. The carbonyl band remaining is significantly narrower than the plasma-treated paint, and the dominant species are the isocyanurate ring with hexamethylene groups and silica. The 3675 cm⁻¹ band due to hydrogen bonding also remains.

At the temperatures to which the sample was exposed (about 800° C), if there were sufficient oxygen available, all of the carbon and hydrogen would have been converted to CO₂ and H₂O. It is interesting that the aliphatic groups survive, and the available oxygen is preferentially consumed by the elimination of urea and amide groups. In contrast, the aliphatic groups of the tan paint are reduced greatly simply by heating in vacuum, and the tan paint was disintegrated upon pyrolysis. Since the pyrolysis experiments are performed in He and the plasma experiments are performed in vacuum, these observations may be simply due to the oxygen balance (i.e., ratio of oxygen to C/H/N) of the tan moisture-cured paint vs. the green water-reducible paint formulations, rather than a much greater resistance of the green paint composition to the plasma. Total oxygen in the cured paint is a complex combination of oxygen from inorganic species such as talc and silica and from organic compounds. The latter can be a function whether the isocyanate remains trapped and how much converts to the amine vs. the urea, or in the two-component paints, how much polyurethane is formed. The amine formation would result in loss of carbon dioxide (e.g., two oxygen atoms) for every amine formed. Future efforts will use oxygen or combinations of oxygen and hydrogen plasmas to facilitate more complete paint removal.

4.3 Summary of FTIR Results. IR spectroscopy, using PAS to probe the bulk spectra and reflectance microspectroscopy to probe the surface layer, was used to characterize two types of



File # 1 = PYROTRG

E:\PAM\REFLECT\PYRO\pyrotrg ax = 0.225983\0.247345

Pyrolyzed plasma-treated sample

Res= 4cm-1

Figure 27. IR Spectrum of the Pyrolysis Residue of the Two-Component Green Paint.

one-component paints—a water-reducible green paint and a moisture-cured tan paint; a green two-component water-reducible paint with polyurethane bonds was also characterized.

The PAS spectra of the tan one-pack moisture-cured paints showed:

- Heating and vacuum alone causes minimal subsurface reaction. The dramatic color change from light tan to brick red is probably due to a change in a pigment chromophore with a very high absorption coefficient in the visible region but present at very low concentration.
- Treatment with the H-plasma and heat eliminates most of the organic material present, such as urea, amines, ethers, and some aliphatic groups. Elimination of urea bonds in these paints is important since they provide polymerization essential to the integrity of the sample. Thus, this paint appears charred after treatment.
- The isocyanurate ring and associated hexamethylene groups survive the plasma treatment. The aliphatic groups associated with the isocyanurate ring are not “unzipped” by the action of the hydrogen plasma. Silica remains after plasma treatment, as expected.

The PAS spectra of the water-reducible one- and two-pack green paints showed that:

- The one-pack paint reflects a distinct band at 1765 cm^{-1} not present in the two-pack paint, probably due to an aromatic ester prepolymer. This band is eliminated upon plasma treatment.
- The carbonyl region of the water-reducible green paints is broader than for the tan paints, reflecting not only the fact that polyurethane forms in the two-component water-reducible paint but that a different polyurethane prepolymer is probably used in the water-reducible and moisture-cured paints.
- The virgin green water-reducible paints both reflect the 2270 cm^{-1} band of the isocyanate monomer, which may be trapped under the surface due to a tight surface “skin” formation. No

monomer remains in the tan moisture-cured paint, possibly because the level of polymerization achieved is less.

The green water-reducible paints were both much more resistant to the plasma treatment than was the tan moisture-cured paint sample. In the green paint samples, the urea and polyurethane remain, as evidenced by the carbonyl and amide II bands, whereas in the tan paints, primarily only the inorganic species and isocyanurate remained. The aliphatic bands were still evident in the tan samples, but were significantly reduced. The aliphatic bands in the green paints were only mildly affected, if at all.

The reflectance spectra of the water-reducible, one- and two-pack green paints show that:

- Unlike the tan moisture-cured paints in which the NH stretch and aliphatic bands at the surface are virtually eliminated by plasma treatment, the green paints exhibit only a modest reduction. Visual inspection of the samples shows that the green samples appear relatively undisturbed by the plasma treatment.
- As with the tan paint, the silica bands are more dominant in the PAS spectra, consistent with their settling during curing.
- Both the reflectance and PAS spectra of the virgin one-pack paint show a high-frequency carbonyl at 1765 cm^{-1} , which is attributed to a phthalate-polyurethane prepolymer. Both spectra show that this band is greatly reduced upon plasma treatment.
- The two-pack paint appears to have relatively less urea than does the one-pack paint, consistent with the fact that the former can form urethane cross-links. The two-pack paint also contains more isocyanate monomer, consistent with its high isocyanate index.

- Upon plasma treatment, the one-pack paint appears to lose isocyanate and urea groups. The spectra of the two-component paint suggests that the isocyanate may cross-link further to form the biuret.
- The two-pack sample has a very sharp, distinct band, due to free hydroxyl groups, at 3675 cm^{-1} , which may be due to a sterically hindered organic hydroxyl-containing compound, or to magnesium silicate.

Mild heat and plasma treatment may be a means of improving paint properties by facilitating reaction of trapped unreacted isocyanate and extending polymerization. The isocyanate might also arise from breakdown of the isocyanurate ring. Mildly treated tan paint samples showed that:

- Mild heat and plasma treatment most likely results in the conversion of amine groups to urea cross-links. The plasma treatment is essential in this conversion; heat treatment alone is not sufficient. Properties that rely on thorough cross-linking, such as adhesion, and resistance to impact, CARC, and corrosion may benefit from improved cross-linking.
- Understanding the role of the isocyanurate monomer in the paint-curing and plasma-treatment processes is critical, since it controls cross-linking and polymerization reactions. It appears that a significant amount (although not all, as evidenced by the relative intensity of isocyanurate bands to that of silica) remains after intense plasma treatment, but some apparently breaks down under mild plasma treatment to provide the monomer for further urea formation. Further clarification of these results is needed.

The reflectance spectra were more sensitive to changes above 3000 cm^{-1} , including those from the aliphatic stretching region, NH/NH₂ bands, and OH groups.

- Heat treatment results in loss of NH/NH₂ groups, probably from amines residue on the surface, and, to a lesser extent, urea groups, as evidenced particularly from bands above 3000 cm^{-1} . Plasma treatment of the samples eliminates much but not all of the organic material. As in the

PAS spectra of the plasma-treated samples, the dominant bands are due to silica and the isocyanurate ring with isocyanurate. The reflectance spectra show that the aliphatic groups at the surface are removed to a greater extent than those in the bulk (shown in the PAS spectra). However, unlike the PAS spectra, some amide, and probably urea, remains in the reflectance spectra.

Pyrolysis of paint samples showed that the tan moisture-cured and green water-reducible paints reacted much differently to pyrolysis (nom. 800° C for 20 s) condition. Whereas the tan paint disintegrated, the green paints appeared visually quite intact. In the green paints, the aliphatic groups survive and the available oxygen is preferentially consumed by the elimination of urea and amide groups. Thus, the greater effectiveness of the plasma in removal of the tan paints may be simply due to a difference in oxygen balance (i.e., ratio of oxygen to C/H/N) of the tan paint vs. the green paint formulations. Removal of these paints by oxygen and/or mixtures of oxygen/hydrogen is being pursued.

Unlike the spectra of the cured paint sample, the spectra of the purple glossy top layer, and homogenized sample of Component A, sampling of Component A layers in two-pack green paint showed distinct bands with clear separation. Polyurethane is present in both these fractions as a prepolymer. The broad bands and sloping baselines obtained in spectra of the cured paint samples, especially in the region between 1000–800 cm^{-1} , may reflect the complexity of the final composition. However, uncured samples from Component A were much more glossy and reflective than in the cured paint sample. Thus, the abnormally high sloping baseline is probably also an artifact of the sample surface morphology as well. Alternative sampling methods will be pursued in the future.

5. Conclusions

In conclusion, cool temperature plasma removal shows promise for military removal of HDI-based paints from metal substrates. The one-pack standard moisture-cured urea paint is removed more readily than the experimental water-reducible paints. The isocyanurate ring with associated

hexamethylene groups and inorganic fill material such as silica and talc survive the plasma treatment in all the paints evaluated. With the one-pack moisture-cured tan paint, the urea groups, which serve to cross-link the polymer, are eliminated and the sample appears charred. Bands due to amide, urea, and polyurethane persist in the spectra of the green water-reducible paints after plasma removal, and the paint appears intact except for a slight darkening of the forest green color. Both the water-reducible paints had unreacted isocyanate groups present in the virgin material; none was detected in the one-pack moisture-cured tan paint. Plasma treatment may actually increase polymerization in the two-component paint by facilitating further reaction to the biuret. Moreover, reaction due to the plasma may be linked to the level of oxygen in the sample. Pyrolysis at 800° C in an inert atmosphere showed that the virgin one-pack moisture-cured tan paint disintegrated, while the water-reducible green paints were much intact. Further studies with oxygen-containing plasmas will be pursued.

Cool temperature plasma paint removal has an important advantage over line-of-sight techniques, such as laser ablation, in that it is effective in difficult-to-access areas such as honeycombs and nonflat interfaces. Since the plasma alone increases the temperature of the sample only about 10–20° C, the likelihood of hydrogen embrittlement is minimized. In the paint removal efforts to date, no testing for embrittlement has been performed.

Mild plasma treatment may be effective in further cross-linking military paints. Mild treatment of the standard moisture-cured paint showed evidence that amine groups were converted to urea. Heat treatment alone did not result in further reaction or paint removal. Paint properties that depend on cross-linking include adhesion and resistance to impact, chemical agents, and corrosion.

6. Future Work

Work is already in progress on using oxygen plasmas for removal of military paints. Paints that will be examined in the future include those with polymer, rather than siliceous, solids fill. Alternative sampling methods will be pursued. Attenuated total reflectance (ATR) could be very powerful in

obtaining high-quality spectra of these materials without the distortions to the baseline observed in reflectance spectra. Also, x-ray and neutron-scattering techniques would be helpful to confirm assignments. Hydrogen embrittlement remains a cause for concern, and future efforts would, ideally, address that issue. Mild plasma treatment, and the effect on mechanical properties of the paint, is also of interest, but not currently scheduled.

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6. AUTHOR(S) P. J. Kaste, R. G. Daniel, R. A. Pesce Rodriguez, M. A. Schroeder, and J. A. Escarsega			
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13. ABSTRACT (Maximum 200 words) A moderate temperature hydrogen plasma has been developed for removal of chemical-agent-resistant (CARC) propellant coatings, and the chemistry and morphology of the CARC removal process has been investigated. A microwave-based plasma generator, producing a low-temperature atomic beam was used to treat the samples. The plasma heats the sample only 10-20° C. Additional heat was supplied to maintain temperatures of 200-300° C. Helium and hydrogen plasmas were studied in this effort. However, helium was not at all effective, showing that atomic bombardment alone is not sufficient to remove the paint, and that chemical reactivity is needed. One of the CARC paints studied, a conventional formulation, is on the qualified products list, while the other two formulations are experimental. Paint variables that were studied include: one- and two-pack formulations; moisture-cured and water-reducible chemistries; aluminum with chromate, and steel with zinc phosphate conversion coatings; and presence or absence of an adhesive epoxy sublayer. The samples were characterized by microreflectance and photoacoustic Fourier-transform infrared spectroscopies. Heat treatment to 300° C resulted in some degradation of the conventional CARC, but the experimental CARC was mostly unaffected. The hydrogen plasma removed up to 50 weight-percent of the CARC layers, but was much more effective in degrading the conventional formulation. Virtually all of the urea, amine, and polyurethane (present in the resin as a prepolymer) functional groups were removed by the H-plasma in the case of the conventional propellant, whereas in the experimental paints, these groups were only slightly reduced.			
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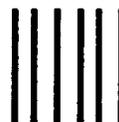
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